Journal of the Chinese Chemical Society, **1994**, *41*, 763-773

Insertion Reactions of Square-Planar Diorganoplatinum. 2.[1] Stereoselective Carbonylation of *trans*-$Pt(R)(R')(PPh_3)_2$ Leading to *cis*-$Pt(R)(COR')(PPh_3)_2$ and Isomers of $Pt(PPh_3)(CO)(COR')(R)^+$

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Synthesis of square-planar trans dialkyl and alkyl aryl complexes of platinum(II), *trans*-$Pt(R)(R')(PPh_3)_2$ (R = Me R′ = Et (**2a**); R = Me R′ = Ph (**2b**); R = R′ = Et (**2c**); R = Et R′ = Ph (**2d**)) was established employing transmetalation of *trans*-$Pt(R)(I)(PPh_3)_2$ with Grignard reagents R′MgX. Complexes **2a**-**2c** underwent stereoselective carbonylation to produce *cis*-$Pt(R)(COR')(PPh_3)_2$ (R = Me R′ = Et (**3a**); R = Me R′ = Ph (**3b**); R = R′ = Et (**3c**)). These facile transformations were exclusive and quantitative. The reactivity of carbonylation followed the order Et > Ph > Me. A similar reaction of **2d** with CO yielded EtC(O)Ph instead. The cis acyl alkyl or acyl aryl complexes **3a**-**3c** suffered substitution of CO for a PPh_3, leading to two isomers *SP*-4-3- and *SP*-4-4-$Pt(PPh_3)(CO)(COR')(R)$ (R = Me R′ = Et (**4a, 4a′**); R = Me R′ = Ph (**4b, 4b′**); R = R′ = Et (**4c, 4c′**)), respectively. The reverse reactions of **4** to **3** readily occurred when external PPh_3 was provided. The stereoselectivity of carbonylation of *trans*-$Pt(R)(R')(PPh_3)_2$ is explained by a mechanism in which reversible displacement of a PPh_3 by CO in the reactant precedes to form a four-coordinate dialkyl carbonyl intermediate $Pt(PPh_3)(CO)(R)(R')$. The ensuing alkyl (or aryl) migration from metal to the carbonyl carbon achieves the cis acyl alkyl (or aryl) configuration. Recoordination of a PPh_3 completes the reaction. X-ray structures of **2b, 2c, 3b** and **4b** as single crystals are provided.

INTRODUCTION

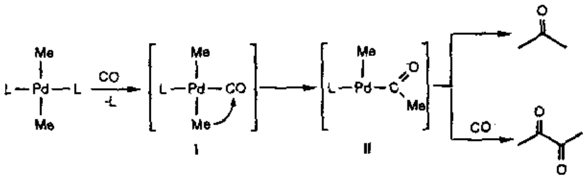
Despite much research on CO insertion of organoplatinum complexes, the chemistry of carbonylation of square-planar diorganoplatinum(II) species is little explored.[2] Chatt and Shaw reported the first synthesis of *cis*-PtR_2L_2 (R = alkyl or aryl; L = monodentate phosphines) in 1959.[3] Such cis diorgano complexes were found to react with CO to cause displacement of a phosphine by CO (eq 1), but no carbonyl insertion.[4]

$$cis\text{-}MR_2L_2 + CO \longrightarrow cis\text{-}MR_2(CO)L + L \qquad (1)$$

(M = Pd, Pt; R = Me, Ph; L = PPh_3, $PMePh_2$, PEt_3)

Yamamoto et al. reported that *trans*-$PdMe_2L_2$ underwent carbonylation to generate ketone and diketone products. A mechanism that comprises a four-coordinate dialkyl carbonyl intermediate (**I**) transforming to a cis acyl alkyl composition (**II**) via migratory CO insertion, was proposed (Scheme I). However, no direct evidence for intermediates was provided.[5] We successfully synthesized diorganoplatinum complexes *trans*-$Pt(COR)(R')(PPh_3)_2$ and *trans*-$Pt(COCOR)(R')(PPh_3)_2$ (R, R′ = alkyl, aryl). Such trans species undergo facile stereoselective carbonylation to give well characterized new cis diorganoplatinum derivatives *cis*-$Pt(COR)(COR')(PPh_3)_2$ and *cis*-$Pt(COCOR)(COR')(PPh_3)_2$, respectively, which also lead to formation of ketones and diketones in the presence of CO.[1] Our results thus afford a perfect model for carbonylation of the trans diorganopalladium system. The trans dialkylplatinum derivatives *trans*-$PtRR'L_2$ are well known,[6] but carbonylation chemistry of these complexes is not yet documented.

Scheme I



Dedicated to Professor Sung-Mao Wang (王松茂) on the occasion of his seventieth birthday.

[+] Based on the M. S. thesis of B.-C. Shu, National Taiwan University, 1992 and the M. S. thesis of T.-M. Huang, National Taiwan University, 1989.

During our preliminary work on nucleophilic addition of MeLi to *cis*-Pt(COPh)(CO)$(PPh_3)_2^+$, *cis*-Pt(Me)(COPh)$(PPh_3)_2$ and *SP*-4-3-Pt(PPh_3)(CO)(COPh)(Me) resulted.[1,7] The cis acyl alkyl species are just the legitimate products of carbonylation of trans dialkylplatinum complexes. In this article, we present our extended work on carbonylation of trans diorganoplatinum(II), specifically *trans*-Pt(R)(R′)$(PPh_3)_2$ (R, R′ = alkyl or aryl). These reactions lead to *cis*-Pt(R)(COR′)$(PPh_3)_2$ and isomers of Pt(PPh_3)(CO)(COR′)(R). Relevant reaction mechanisms are discussed. The X-ray structures of single-crystals of the title complexes are provided.

RESULTS AND DISCUSSION

Synthesis and Characterization of *trans*-Pt(R)(R′)$(PPh_3)_2$

Treatment of *trans*-Pt(Me)(I)$(PPh_3)_2$ **(1a)** with EtMgBr or PhMgCl in benzene at 25 °C under dry nitrogen resulted in *trans*-Pt(R)(R′)$(PPh_3)_2$ (R = Me R′ = Et **(2a)**; R = Me R′ = Ph **(2b)**) (eq 2). Analogous reaction of *trans*-Pt(Et)(I)$(PPh_3)_2$ **(1b)** and EtMgBr at 45 °C afforded *trans*-Pt$(Et)_2(PPh_3)_2$ **(2c)** (eq 3). *trans*-Pt(Et)(Ph)$(PPh_3)_2$ **(2d)** was obtained from the reaction of **1b** with PhMgCl in benzene under refluxing conditions (eq 4). The products generally contain crossed organohalo complexes *trans*-Pt(R)(X)$(PPh_3)_2$ (in which R and X may originate from either the starting complex or the Grignard reagent), which may cause unsatisfactory purification of the desired derivatives. Vigorous stirring typically led to less desired crossed products of *trans*-Pt(R)(X)$(PPh_3)_2$. For instance, instead of **2d**, the heavily stirred reaction of Eq 4 gave *trans*-Pt(Ph)(I)$(PPh_3)_2$ **(1c)**. The acetylide derivative *trans*-Pt(Me)(C≡CPh)$(PPh_3)_2$ **(2e)** was prepared by reaction of **1a** and phenylacetylene at 60 °C with the assistance of excess Et_2NH (eq 5).[8]

$$trans\text{-Pt(Me)(I)(PPh}_3)_2 + \text{RMgX} \xrightarrow[25\ ^\circ\text{C}]{\text{benzene}} trans\text{-Pt(Me)(R)(PPh}_3)_2 + \text{Mg(X)(I)} \qquad (2)$$

R = Et **2a**, Ph **2b**

$$trans\text{-Pt(Et)(I)(PPh}_3)_2 + \text{EtMgBr} \xrightarrow[45\ ^\circ\text{C}]{\text{benzene}} trans\text{-Pt(Et)}_2\text{(PPh}_3)_2 + \text{Mg(Br)(I)} \qquad (3)$$

2c

$$trans\text{-Pt(Et)(I)(PPh}_3)_2 + \text{PhMgCl} \xrightarrow[\text{reflux}]{\text{benzene}} trans\text{-Pt(Et)(Ph)(PPh}_3)_2 + \text{Mg(Cl)(I)} \qquad (4)$$

2d

$$trans\text{-Pt(Me)(I)(PPh}_3)_2 + \text{PhC}\equiv\text{CH} \xrightarrow[60\ ^\circ\text{C}]{\text{Et}_2\text{NH}} trans\text{-Pt(Me)(C}\equiv\text{CPh)(PPh}_3)_2 + \text{Et}_2\text{NH}_2\text{(I)} \qquad (5)$$

2e

When organolithium RLi (R = Me or Ph) was used as alkylating reagents to react with **1a-c**, cis dialkyl complexes *cis*-Pt$(R)_2(PPh_3)_2$ were obtained. The reaction of **1a** with equimolar proportions of Et_2Zn yielded the cis diethyl product *cis*-Pt$(Et)_2(PPh_3)_2$. Our attempts to prepare the trans dimethyl complex according to a similar procedure were unsuccessful. Treatment of **1a** or *trans*-Pt(Me)$(OSO_2CF_3)(PPh_3)_2$ with MeMgCl resulted only *cis*-Pt$(Me)_2(PPh_3)_2$.

Trans diorgano complexes **2a-d** generally show characteristic $^2J_{Pt\text{-}H}$ in the range 45-50 Hz. The structure of **2b** and **2c** as single-crystals were determined by X-ray diffraction. Their ORTEP drawings appear in Fig. 1. Both complexes were in trans square-planar geometry. In the crystal of **2b**, solvent molecules of CH_2Cl_2 are disordered. The plane of the phenyl ligand and the molecular plane constitute a dihedral angle 98.3 (5)°. Complex **2c** has C_2 symme-

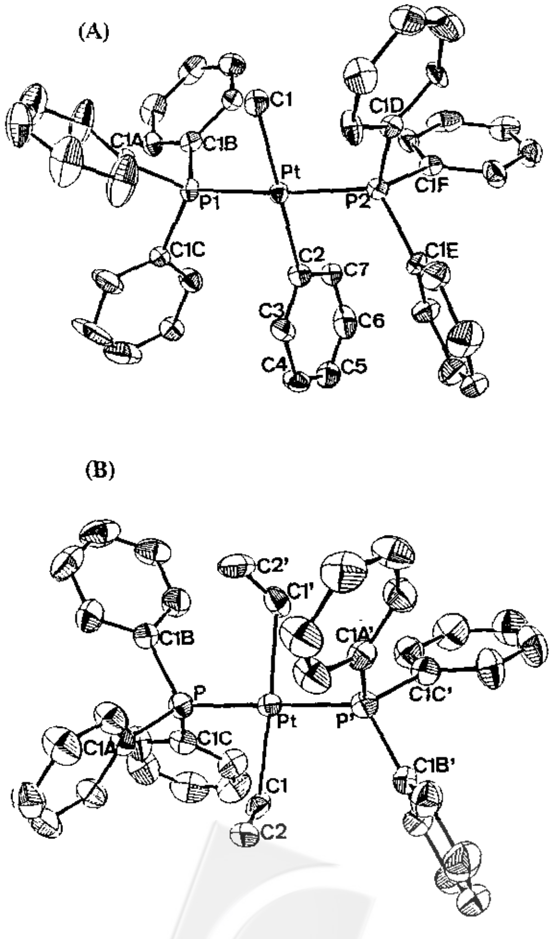


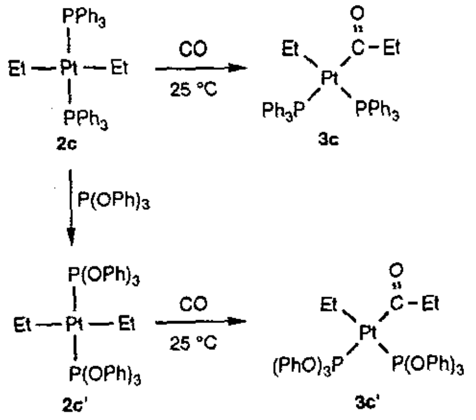
Fig. 1. ORTEP drawings of (a) *trans*-Pt(Me)(Ph)$(PPh_3)_2$ **(2b)** (b) *trans*-Pt$(Et)_2(PPh_3)_2$ **(2c)** (all hydrogen atoms are ommitted for clarity.)

try with the rotational axis passing through the metal center and being perpendicular to the molecular plane. The torsional angle between the two ethyl ligands is 35.4°. The dihedral angle between the Pt-C1-C2 plane and the molecular plane is 72.32 (5)°.

Formation of *cis*-Pt(R)(COR′)(PPh$_3$)$_2$ via Stereoselective Carbonylation of *trans*-Pt(R)(R′)(PPh$_3$)$_2$

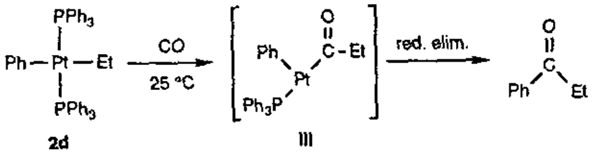
The reaction of *trans*-Pt(Et)$_2$(PPh$_3$)$_2$ (**2c**) and CO in d$_6$-benzene at 25 °C generated a single product (designated **3c**) in quantitative yield within the first NMR measurement. The ^{31}P NMR spectrum of this new compound **3c** exhibits a doublet of doublets with chemical shifts and coupling constants δ 18.9 ($^1J_{P\text{-}Pt}$ = 1253 Hz) and 22.0 ($^1J_{P\text{-}Pt}$ = 2035 Hz), indicating that such a compound contains two magnetically inequivalent phosphorus atoms. These data may be explained according to a cis square-planar structure with two phosphines trans to an acyl and an alkyl ligand, respectively.[1] The ^{1}H NMR spectrum shows two sets of ethyl signals (each consisting of a triplet and a quartet) at δ 0.97, 1.35 and 1.66, 2.61, respectively, with the one at δ 1.35 having the large value of $^2J_{H\text{-}Pt}$ = 78 Hz, supporting the existence of an ethyl ligand and a propanoyl ligand in **3c**. The propanoyl C=O line in the infrared spectrum was observed at 1623 cm^{-1}. Complex **3c** is thus identified as *cis*-Pt(Et)(COEt)(PPh$_3$)$_2$. Treatment of **2c** with 3 equiv. of P(OPh)$_3$ resulted in phosphite derivative *trans*-Pt(Et)$_2$[P(OPh)$_3$]$_2$ (**2c′**) which underwent analogous carbonylation to form *cis*-Pt(Et)(COEt)[P(OPh)$_3$]$_2$ (**3c′**) (Scheme II).

Scheme II



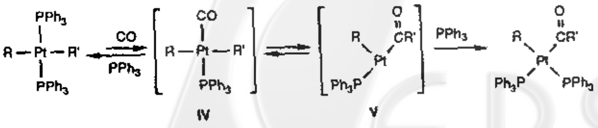
As for the reactivity of carbonylation of the asymmetric dialkyl derivatives, the reaction of *trans*-Pt(Me)(Et)(PPh$_3$)$_2$ (**2a**) with CO in d$_6$-benzene at 25 °C was found to result first in a cis derivative (**3a**) as the only product. Its ^{31}P NMR signals were located at δ 18.0 ($J_{P\text{-}P}$ = 11.5 Hz, $J_{P\text{-}Pt}$ = 1220 Hz) and 23.4 ($J_{P\text{-}P}$ = 11.5 Hz, $J_{P\text{-}Pt}$ = 2288 Hz). Accordingly, the former is assigned to PPh$_3$ trans to the acyl ligand and the latter to PPh$_3$ trans to the alkyl ligand. The ^{1}H NMR spectrum of **3a** comprises a signal at δ 1.01 due to three protons in a pattern of a doublet of doublets with ^{1}H-^{195}Pt satellites, and a set of ethyl signals at δ 0.96 (triplet) and 2.53 (quartet) in ratio 3:2. The coupling constants of the former signal (δ 1.01) are resolved as $^3J_{H\text{-}P(trans)}$ = 6.2, $^3J_{H\text{-}P(cis)}$ = 9.7 Hz and $^2J_{H\text{-}Pt}$ = 70 Hz. Such data unequivocally indicated that **3a** consists of a methyl and a propanoyl ligands. Complex **3a** is identified as *cis*-Pt(Me)(COEt)(PPh$_3$)$_2$. Another possible product of carbonylation of **2a** *cis*-Pt(Et)(COMe)(PPh$_3$)$_2$, was never attained. In contrast to the forementioned two ethyl derivatives, *trans*-Pt(Et)(Ph)(PPh$_3$)$_2$ (**2d**) and CO rapidly resulted in PhC(O)Et under the same conditions, presumably via reductive elimination of a phenyl propanoyl intermediate **III** as shown in Scheme III. The reaction of *trans*-Pt(Me)(Ph)(PPh$_3$)$_2$ (**2b**) with CO analogously provided only one product *cis*-Pt(Me)(COPh)(PPh$_3$)$_2$ (**3b**) in which CO was incorporated on the phenyl ligand. The overall reaction was much slower than carbonylation of the ethyl derivatives. The acetylide methyl complex **2e** failed to react with CO under the same conditions.

Scheme III



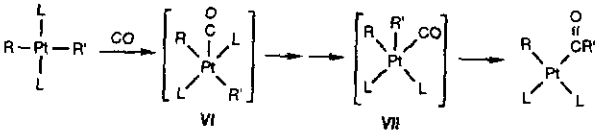
For the products from carbonylation reactions of *trans*-Pt(R)(R′)(PPh$_3$)$_2$, the reactivity of carbonylation followed the order Et > Ph > Me. Such a series of reaction rate and stereoselectivity of trans-to-cis transformation are the same as those found in carbonylation reactions of *trans*-Pt(COR)(R′)(PPh$_3$)$_2$ and *trans*-Pt(COCOR)(R′)(PPh$_3$)$_2$.[1] The same order of reactivity was previously observed in the carbonylation reactions of other metal systems.[10] A mechanism as depicted in Scheme IV provides plausible explanations. Leading displacement of a PPh$_3$ ligand in *trans*-Pt(R)(R′)(PPh$_3$)$_2$ by CO first causes a four-coordinate intermediate **IV** in which the entering carbonyl ligand is cis to

Scheme IV



both alkyl ligands. An ensuing alkyl migration from metal to the carbonyl carbon results in the cis acyl alkyl configuration (intermediate **V**). Coordination of a PPh_3 to the three-coordinate **V** then achieves *cis*-Pt(R)(COR′)$(PPh_3)_2$. The reaction steps of ligand substitution and alkyl migration are both likely reversible. Deliberately added PPh_3 to the system inhibited the carbonylation. The exceptional reactivity of carbonylation is ascribed to the decarbonylation of the acyl group in **V**, reverting to **IV**, following the order C(O)Me > C(O)Ph > C(O)Et.[1] The mechanism in Scheme III is consistent with Yamamoto's rationale about the carbonylation of trans dialkylpalladium. Furthermore, the platinum system provides mechanistic evidence and serves as an excellent model for the palladium system. An alternative mechanism involving five-coordinate intermediates such as **VI** and **VII** etc. shown in Scheme V perhaps should not be arbitrarily excluded, although the necessary multistep ligand rearrangement would account for the exclusive product and its stereoselectivity with difficulty.

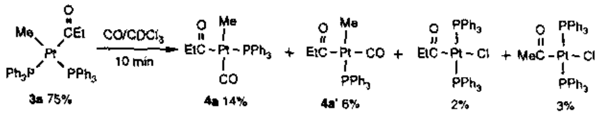
Scheme V



Reactions of *cis*-Pt(R)(COR′)$(PPh_3)_2$ with CO

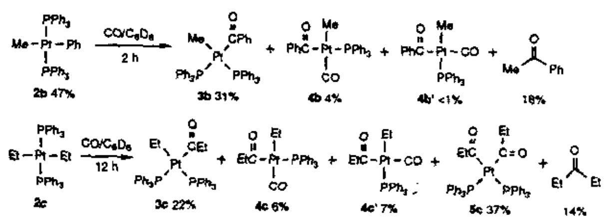
When *cis*-Pt(Me)(COEt)$(PPh_3)_2$ (**3a**) and CO were allowed to stand for 10 min in $CDCl_3$ at 25 °C, the ^{31}P NMR spectrum indicated that the system generated two new inorganic species and two known acylchloro complexes *trans*-Pt(COEt)(Cl)$(PPh_3)_2$ and *trans*-Pt(COMe)(Cl)$(PPh_3)_2$. Each of the two new compounds may contain a phosphine trans to an acyl ligand (δ 17.0, $J_{P\text{-}Pt} = 1285$ Hz, designated as **4a**) or to an alkyl ligand (δ 20.7, $J_{P\text{-}Pt} = 2021$ Hz, designated as **4a′**), respectively. The relative abundance of **4a** and **4a′** was about 2:1. The ^1H NMR spectrum of the mixture of **4a** and **4a′** indicated that each of the two complexes likely comprises a methyl ligand (δ 0.43, $^3J_{H\text{-}P(cis)} = 10.4$ Hz; $^2J_{H\text{-}Pt} = 71.1$ Hz; δ 0.88, $^3J_{H\text{-}P(trans)} = 6.1$ Hz, $^2J_{H\text{-}Pt} = 74.3$ Hz) and a propanoyl ligand (δ 1.23 (t), 2.68 (q); δ 0.67 (t), 1.97 (q)). Two terminal carbonyls show their independent stretching absorption lines at 2041 and 2075 cm^{-1} in the infrared spectrum. Accordingly, complexes **4a** and **4a′** are identified as *SP*-4-3- and *SP*-4-4-Pt(PPh_3)(CO)(COEt)(Me). The total conversion was 25% and the relative abundance of each species have been shown in Scheme VI. When the mixtures were left long in solution, 2-butanone and the two acylhalo species increased at the expense of **3a, 4a** and **4a′**.

Scheme VI



Reaction of **2b** with CO in d_6-benzene at 25 °C for 2 h resulted in three major inorganic species identified as *cis*-Pt(COPh)(Me)$(PPh_3)_2$ (**3b**), *SP*-4-3- and *SP*-4-4-Pt(PPh_3)-(CO)(COPh)(Me) (**4b** and **4b′** respectively). 47% of starting **2b** was left unreacted; the relative yields of the carbonylated complexes **3b, 4b**, and **4b′** were 0.31 : 0.04 : < 0.01. No acylhalo complex was ever observed in such a case, however, substantial acetophenone (18% based on ^1H NMR integration) was detected then. In the reaction of **2c** with CO, the relative yields of *cis*-Pt(COEt)(Et)$(PPh_3)_2$ (**3c**), *SP*-4-3- and *SP*-4-4-Pt(PPh_3)(CO)(COEt)(Et) (**4c** and **4c′** respectively), *cis*-Pt$(COEt)_2(PPh_3)_2$ (**5c**), and EtC(O)Et reached 0.22:0.06:0.07:0.37:0.14 after reaction in d_6-benzene at 25 °C for 12 h (Scheme VII).

Scheme VII



Complexes **3b** and **4b** were previously obtained from nucleophilic addition of MeLi to *cis*-Pt(COPh)(CO)$(PPh_3)_2^+$ ion and exhibited consistent spectral data. In addition, their molecular structures have been determined by X-ray diffraction of single-crystals, which unequivocally confirm our identifications. Fig. 2 and 3 display ORTEP drawings of **3b** and **4b** respectively. The four ligands of **3b** constitute a distorted square-planar geometry. The benzoyl and methyl ligands are in cis positions with ∠C-Pt-C1 being 80.9 (4)°; ∠P1-Pt-P2 thus is widened to 99.5 (1)°. In the cis square-planar configuration of **3b**, the Pt-P1 bond of the phosphine trans to the methyl group is 0.059 (6) Å shorter than the Pt-P2 bond trans to the benzoyl group. This result agrees with our previous assertion that the trans influence of -C(O)Ph is larger than that of $-CH_3$.[1,9] Complex **4b** consists of terminal carbonyl, methyl, benzoyl, and triphenylphosphine ligands that are arranged in a square plane. The π-acid carbonyl and the electron withdrawing benzoyl group are respectively located at the trans positions to the electron-releasing methyl and phosphine. Such a feature explains the greater stability of **4b** than of **4b′**. **4b** contains metal-carbon single bonds of three types on the same metal, which show increasing order of Pt-C(*sp*) = 1.897 (7) < Pt-C(sp^2) = 2.064 (6) < Pt-C(sp^3) = 2.108 (7).

The formation of **4c** and **4c′** was also examined by a direct approach from the reaction of **3c** and CO, which has provided a more explicit picture. A sample of isolated **3c** was dissolved in CO-saturated d_6-benzene at 5 °C. Complexes **4c** and **4c′** were formed immediately. Their total amount first increased at the expense of **3c** to about 40% total conversion, but decreased later. Then *cis*-Pt(COEt)$_2$-(PPh$_3$)$_2$ (**5c**) and EtC(O)Et were observed and continued to increase thereafter. A two-dimensional H-H COSY spectrum of such a mixture appears in Fig. 4. When the reaction was undertaken in the presence of sulfur (serving as phosphine scavenger), the conversion of **3c** to **4c** and **4c′** was nearly complete within the first NMR measurement. Meanwhile, stoichiometric Ph$_3$PS was formed. In general, displacement of PPh$_3$ which is trans to the acyl ligand in **3** could be kinetically preferred, as acyl has a larger trans influence than alkyl. However, the resulting **4′** (in which acyl and carbonyl are trans to each other) eventually transforms to the thermodynamically more stable species **4** (in which the π-acid carbonyl is trans to the electron-donating alkyl) via **3** by reverting substitution (Scheme VIII). The phosphite derivative *cis*-Pt(Et)(COEt)[P(OPh)$_3$]$_2$ (**3c′**) was found unreactive to CO under the same conditions. The inertness of **3c′** to CO is ascribed to that the more electron-withdrawing phosphite would disfavor the coordination of π-acid ligand like CO. The exact mechanistic route for the occurrence of **5c** is unclear. In view of the lack of other inorganic products at the final stage, formation of **5c** may be a thermodynamic outcome of complicated transformations.

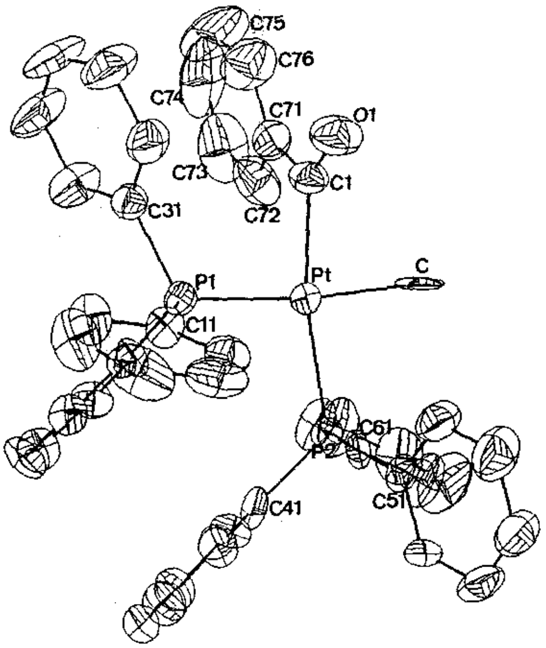


Fig. 2. ORTEP drawing of *cis*-Pt(COPh)(Me)(PPh$_3$)$_2$ (**3b**) (all hydrogen atoms are ommitted for clarity.)

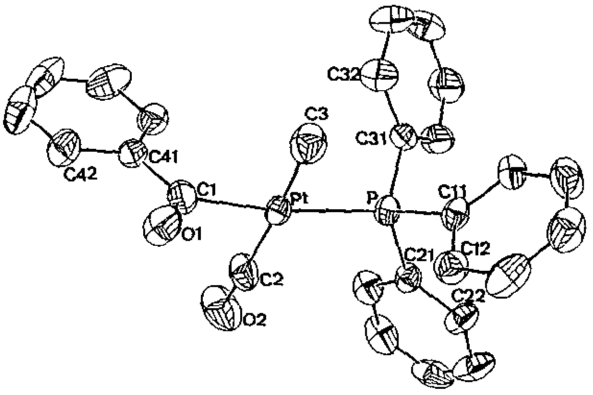


Fig. 3. ORTEP drawing of *SP*-4-3-Pt(PPh$_3$)(CO)-(COPh)(Me) (**4b**) (all hydrogen atoms are ommitted for clarity.)

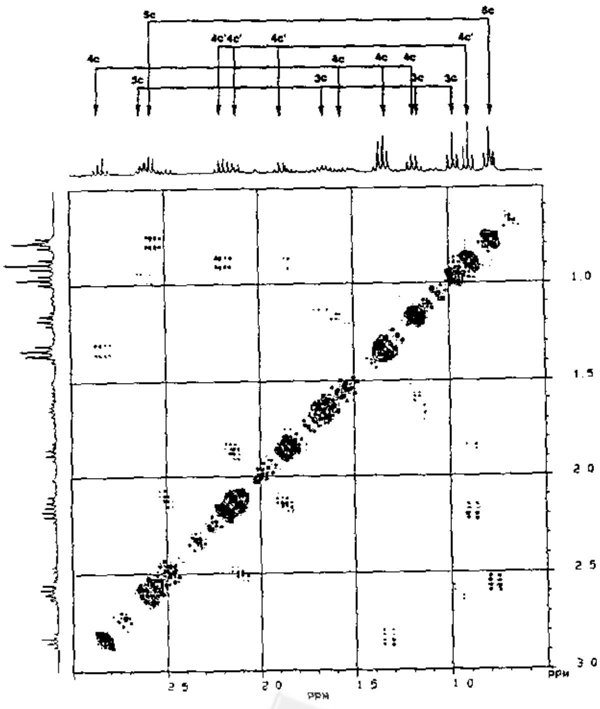
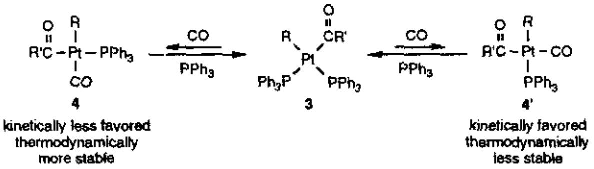


Fig. 4. 2D H-H COSY NMR spectrum for reaction of *cis*-Pt(COEt)(Et)(PPh$_3$)$_2$ (**3c**) with CO, yielding *SP*-4-3-, *SP*-4-4-Pt(PPh$_3$)(CO)(COEt)(Et) (**4c** and **4c′**), and *cis*-Pt(COEt)$_2$(PPh$_3$)$_2$ (**5c**).

Scheme VIII



CONCLUSIONS

Like other trans square-planar diorganoplatinum(II) species such as *trans*-Pt(COR)(R′)$(PPh_3)_2$ and *trans*-Pt(CO-COR)(R′)$(PPh_3)_2$, *trans*-Pt(R)(R′)$(PPh_3)_2$ are subject to carbonylation to form cis derivatives *cis*-Pt(COR′)(R)-$(PPh_3)_2$; the reactions are quantitative. The reactivity of carbonylation follows the order Et >> Ph >> Me, so that has been only a single product from each reaction. Such carbonylations appear to proceed via a four-coordinate dialkyl carbonyl intermediate, and provide a stoichiometric model for carbonylation of trans square-planar diorganopalladium(II) systems. In the presence of CO (1 atm), complexes *cis*-Pt(COR′)(R)$(PPh_3)_2$ are transformed to *SP*-4-3- and *SP*-4-4-Pt(PPh_3)(CO)(COR′)(R) by substitution of CO for a PPh_3. The former are thermodynamically favored, in which both π-acid ligands, acyl and CO, are trans to electron-donating groups, PPh_3 and alkyl, respectively. Cis acyl alkyl species may decompose to organic ketone products via reductive coupling processes.

EXPERIMENTAL SECTION

General

Starting complexes *trans*-Pt(R)(I)$(PPh_3)_2$ (R = Me, Et) were prepared according to literature methods.[1] Commercially available reagents were used without further purification unless otherwise indicated. Benzene, toluene, hexane, diethyl ether and tetrahydrofuran were distilled from purple solutions of benzophenone ketyl under nitrogen, and methylene dichloride, chloroform and acetonitrile were dried with P_2O_5 and distilled immediately before use. Air-sensitive material was manipulated in a nitrogen atmosphere by glove box or standard Schlenk techniques. Characterizations mainly relied on spectral methods. IR spectra were recorded on a Perkin-Elmer 983G or a Bio-Rad FTS-40 spectrophotometer. NMR spectra were measured on either a Bruker ACE-200 or a Bruker ACE-300 spectrometer. For ^{31}P NMR spectra, the spectrometer frequency 81.015 MHz or 121.49 MHz was employed respectively; the corresponding frequencies for ^{13}C NMR spectra were 50.324 MHz or 75.469 MHz respectively. The chemical shifts of ^{31}P data are given in ppm (δ) relative to 85% H_3PO_4 either in $CDCl_3$ or in d_6-benzene. Values of decreased chemical shift relative to the standard are defined as negative. Data of elemental analysis are unavailable, generally because of mixed products and unsatisfactory purification.

Synthesis and Characterization

***trans*-Pt(Me)(Et)$(PPh_3)_2$ (2a)**

Into a round bottom flask (25 mL) was placed *trans*-Pt(Me)(I)$(PPh_3)_2$ (100 mg, 0.12 mmol). The flask was first charged with N_2-degassed benzene (20 mL), followed with EtMgBr solution (0.24 mL, 1 M in THF). The solution was mildly stirred at 25 °C, then dried in vacuum. Introduction of hexane to the solution caused precipitation of white solids (46 mg) that comprised the desired product (85%) and starting material *trans*-Pt(Et)(I)$(PPh_3)_2$ (15%) and diethyl derivative in a small proportion. The relative yields were based on NMR integration. Further purification for **2a** by recrystallization was unsatisfactory. ^{31}P NMR (C_6D_6) δ 35.0 ($J_{P\text{-}Pt}$ = 3364 Hz); ^1H NMR (C_6D_6) δ 0.14 (3H, t, $J_{H\text{-}P}$ = 5.9 Hz, $J_{H\text{-}Pt}$ = 46.2 Hz, CH_3 (Me)), 0.87 (3H, t, $J_{H\text{-}H}$ = 7.0 Hz, $J_{H\text{-}Pt}$ = 30.5 Hz, CH_2CH_3), δ 0.97 (2H, q, $J_{H\text{-}H}$ = 7.0 Hz, CH_2CH_3). Uncharacteristic phenyl resonances (which are two broad bands in the region of δ 7.2-7.8) are omitted, so are other complexes.

***trans*-Pt(Me)(Ph)$(PPh_3)_2$ (2b)**

Into a round bottom flask, was placed *trans*-Pt(Me)(I)$(PPh_3)_2$ (200 mg, 0.23 mmol). The flask was first charged with N_2-degassed benzene (20 mL), followed by PhMgCl solution (0.23 mL, 0.46 mmol). The solution was mildly stirred at 25 °C, then stood for 2 h to allow complete precipitation of Mg(Cl)(I). The solution was filterted into methanol/hexane result in white solids. The product was collected and washed with ethanol. The yield was 69% (130 mg). Single crystals suitable for X-ray diffraction were grown from CH_2Cl_2/Et_2O. ^{31}P NMR (C_6D_6) δ 28.2 ($J_{P\text{-}Pt}$ = 3224 Hz); ^1H NMR (C_6D_6) δ 0.21 (3H, t, $J_{H\text{-}P}$ = 6.1 Hz, $J_{H\text{-}Pt}$ = 45.4 Hz, CH_3), 6.64 (3H, m, *m,p*-phenyl), 7.26 (2H, m, $J_{H\text{-}Pt}$ ~ 40 Hz, *o*-phenyl).

***trans*-Pt$(Et)_2(PPh_3)_2$ (2c)**

A benzene solution (20 mL) containing **1b** (100 mg, 0.12 mmol) and EtMgBr solution (0.36 mL, 0.36 mmol) was mildly stirred at 45 °C for 15 min, then stood at 25 °C for 2 h. The solution was concentrated in vacuo. Addition of hexane resulted in white solids. The product was washed with ethanol and collected in 58% (50 mg) yields. Single crystals suitable for X-ray diffraction were grown from $CHCl_3/Et_2O$. ^{31}P NMR (C_6D_6) δ 34.6 ($J_{P\text{-}Pt}$ = 3472 Hz); ^1H NMR (C_6D_6) δ 0.85 (6H, t, $J_{H\text{-}H}$ = 7.2 Hz, CH_2CH_3), 1.0 (4H, q, $J_{H\text{-}H}$ = 7.2 Hz, CH_2CH_3).

***trans*-Pt(Et)$_2$[P(OPh)$_3$]$_2$ (2c′)**

Into a d_6-benzene solution containing **2c** was added 3 equiv of $P(OPh)_3$ at 25 °C. Complex **2c** was identified from NMR spectra. ^{31}P NMR (C_6D_6) δ 109.6 ($J_{P\text{-}Pt}$ = 5691 Hz); ^1H NMR (C_6D_6) δ 1.59 (6H, unresolved, CH_2CH_3), 1.50 (4H, unresolved, CH_2CH_3).

***trans*-Pt(Et)(Ph)(PPh$_3$)$_2$ (2d)**

A benzene solution (20 mL) containing **1b** (80 mg, 0.09 mmol) was heated to boil. Slowly injected PhMgCl solution (1.0 M, 0.09 mL, 0.18 mmol). Vigorous stirring was avoid, lest undesired *trans*-Pt(Ph)(I)$(PPh_3)_2$ should be formed. The solution was kept boiled for 1 h and cooled to 25 °C. It was then concentrated in vacuo. Addition of hexane resulted in white solids. The product was washed with ethanol and collected in 56% (40 mg) yields. ^{31}P NMR (C_6D_6) δ 28.0 ($J_{P\text{-}Pt}$ = 3324 Hz); ^1H NMR (C_6D_6) δ 0.85 (3H, t, $J_{H\text{-}H}$ = 7.0 Hz, $J_{H\text{-}Pt}$ = 47.1 Hz, CH_2CH_3), 1.0 (2H, q, $J_{H\text{-}H}$ = 7.0 Hz, CH_2CH_3).

***trans*-Pt(Me)(C≡CPh)(PPh$_3$)$_2$ (2e)**

Complex **2e** was prepared according to a literature procedure.[1] **1a** and phenylacetylene in equimolar proportions and excess Et_2NH were mixed and allowed to react at 60 °C under nitrogen. IR (KBr pellet) $\nu_{C\equiv C}$ 2108 cm^{-1}; ^{31}P NMR ($CDCl_3$) δ 27.0 ($J_{P\text{-}Pt}$ = 2991 Hz). ^1H NMR ($CDCl_3$) δ -0.42 (3H, t, $J_{H\text{-}P}$ = 6.4 Hz, $J_{H\text{-}Pt}$ = 53.6 Hz, CH_3), 6.37, 6.87 (3H, m, *m,p*-phenyl), 7.26 (2H, m, *o*-phenyl).

***cis*-Pt(Me)(COEt)(PPh$_3$)$_2$ (3a)**

Into a solution of CO-saturated benzene (2 mL), was dissolved **2a** (40 mg); the sample contained *trans*-Pt(Et)(I)$(PPh_3)_2$. The solution was cooled to crystallize the white product. A final yield of **3a** (of 14 mg) was recovered after recrysallization from CH_2Cl_2/Et_2O. IR (KBr pellet) ν_{CO} 1627 cm^{-1}; ^{31}P NMR ($CDCl_3$) δ 19.4 (d, $J_{P\text{-}P}$ = 14.7 Hz, $J_{P\text{-}Pt}$ = 1273 Hz), 24.6 (d, $J_{P\text{-}P}$ = 14.7 Hz, $J_{P\text{-}Pt}$ = 2261 Hz); ^1H NMR ($CDCl_3$) δ 0.46 (3H, dd, $J_{H\text{-}P}$ = 6.1, 9.4 Hz, $J_{H\text{-}Pt}$ = 69.6 Hz, CH_3), 0.77 (3H, t, $J_{H\text{-}H}$ = 7.3 Hz, CH_2CH_3), 2.23 (2H, q, $J_{H\text{-}H}$ = 7.3 Hz, CH_2CH_3).

***cis*-Pt(Me)(COPh)(PPh$_3$)$_2$ (3b)**

Into a CO-saturated benzene (5 mL) was dissolved **2c** (200 mg); the sample contained impurity of *trans*-Pt(Et)(I)$(PPh_3)_2$. Addition of hexane to the reaction solution gave white solids. Alternatively, *cis*-[Pt(COPh)(CO)$(PPh_3)_2$](BF_4) was first prepared in situ by treating *trans*-Pt(COCOPh)(Cl)$(PPh_3)_2$ (200 mg, 0.23 mmol) with $AgBF_4$ in equimolar proportions in CH_2Cl_2 at -29 °C. Careful control of temperature was necessary to avoid facile isomerization of *cis*-[Pt(COPh)(CO)$(PPh_3)_2$](BF_4) to its thermodynamically stable trans isomer. After removal of AgCl precipitate by filtration, the temperature of the solution was decreased to -63 °C. To the solution, was added 1.1 equiv of MeLi (as solution in C_6H_{12}/Et_2O) and 1.1 equiv of PPh_3. The reaction solution was concentrated. Et_2O was then introduced to the solution to precipitate yellow solids. Single crystals of **3b** suitable for X-ray diffraction were grown from C_6H_6/Et_2O. IR (KBr pellet) ν_{CO} 1604 cm^{-1}; ^{31}P NMR ($CDCl_3$) δ 20.04 (d, $J_{P\text{-}P}$ = 14.2 Hz, $J_{P\text{-}Pt}$ = 1423 Hz), 24.4 (d, $J_{P\text{-}P}$ = 14.2 Hz, $J_{P\text{-}Pt}$ = 2196 Hz); ^1H NMR ($CDCl_3$) δ 0.33 (3H, dd, $J_{H\text{-}P}$ = 6.1, 9.3 Hz, $J_{H\text{-}Pt}$ = 68.4 Hz, CH_3).

***cis*-Pt(Et)(COEt)(PPh$_3$)$_2$ (3c)**

Into a CO-saturated benzene (5 mL) was dissolved **2c** (200 mg); the sample contained impurity of *trans*-Pt(Et)(I)$(PPh_3)_2$. Addition of hexane to the reaction solution resulted in a white precipitate; the yield was 53% (110 mg). IR (KBr pellet) ν_{CO} 1623 cm^{-1}; ^{31}P NMR (C_6D_6) δ 18.9 (d, $J_{P\text{-}P}$ = 11.4 Hz, $J_{P\text{-}Pt}$ = 1253 Hz), 22.0 (d, $J_{P\text{-}P}$ = 11.4 Hz, $J_{P\text{-}Pt}$ = 2035 Hz); ^1H NMR (C_6D_6) δ 0.97 (3H, t, $J_{H\text{-}H}$ = 7.2 Hz, $COCH_2CH_3$), 1.35 (3H, t, $J_{H\text{-}H}$ = 7.4 Hz, $J_{H\text{-}P}$ = 7.3 Hz, $J_{H\text{-}Pt}$ = 78 Hz, CH_2CH_3), 1.66 (2H, m, unresolved CH_2CH_3), 2.61 (2H, q, $J_{H\text{-}H}$ = 7.2 Hz, $J_{H\text{-}Pt}$ = 33 Hz, $COCH_2CH_3$).

***cis*-Pt(Et)(COEt)[P(OPh)$_3$]$_2$ (3c′)**

Bubbling CO through a d_6-benzene solution of **2c′** immediately resulted in formation of **3c′**. Complex **3c′** in solution was characterized by IR and NMR spectra; isolation of **3c′** was not attempted. IR (C_6D_6) ν_{CO} 1635 cm^{-1}; ^{31}P NMR (C_6D_6) δ 115.6 (d, JP-P= 27 Hz, $J_{P\text{-}Pt}$ = 2317 Hz), 121.3 (d, $J_{P\text{-}P}$ = 27 Hz, $J_{P\text{-}Pt}$ = 3218 Hz); ^1H NMR (C_6D_6) δ 0.88 (2H, t, $J_{H\text{-}H}$ = 7.6 Hz, $J_{H\text{-}P}$ = 12.4 Hz, $J_{H\text{-}Pt}$ = 90.7 Hz, CH_2CH_3), 1.27 (2H, unresolved CH_2CH_3), 1.28 (3H, dt, $J_{H\text{-}H}$ = 7.3 Hz, $COCH_2CH_3$), 2.72 (2H, q, $J_{H\text{-}H}$ = 7.3 Hz, $COCH_2CH_3$).

***SP*-4-3-Pt(PPh$_3$)(CO)(COEt)(Me) (4a) and *SP*-4-4-Pt(PPh$_3$)(CO)(COEt)(Me) (4a′)**

Complexes **4a** and **4a′** resulted from reaction of **3a** and CO and were identified by NMR techniques. **For 4a**: IR ($CDCl_3$) ν_{CO} 1624, 2041 cm^{-1}; ^{31}P NMR ($CDCl_3$) δ 17.0 ($J_{P\text{-}Pt}$ = 1285 Hz); ^1H NMR ($CDCl_3$) δ 0.43 (3H, d, $J_{H\text{-}P}$ = 10.4 Hz, $J_{H\text{-}Pt}$ = 71.1 Hz, CH_3), 1.23 (3H, t, $J_{H\text{-}H}$ = 7.5 Hz, CH_2CH_3), 2.68 (2H, q, $J_{H\text{-}H}$ = 7.5 Hz, CH_2CH_3). **For 4a′**: IR ($CDCl_3$) ν_{CO} 1624, 2075 cm^{-1}; ^{31}P NMR ($CDCl_3$) δ 20.7 ($J_{P\text{-}Pt}$ = 2021 Hz); ^1H NMR ($CDCl_3$) δ 0.67 (3H, t, $J_{H\text{-}H}$ = 7.2 Hz, CH_2CH_3), 0.88 (3H, d, $J_{H\text{-}P}$ = 6.1 Hz, $J_{H\text{-}Pt}$ ~ 74 Hz, CH_3), 1.97 (2H, q, $J_{H\text{-}H}$ = 7.2 Hz, CH_2CH_3).

***SP*-4-3-Pt(PPh$_3$)(CO)(COPh)(Me) (4b) and *SP*-4-4-Pt(PPh$_3$)(CO)(COPh)(Me) (4b′)**

Complexes **4b** and **4b′** resulted from reaction of **3b** and CO and were characterized by NMR techniques. Alternatively, the reaction of *cis*-[Pt(COPh)(CO)$(PPh_3)_2$](BF_4) (see procedure of **3b**) with MeLi in equimolar proportions (as solution in C_6H_{12}/Et_2O) in CH_2Cl_2 at -60 °C led to mixed products **3b, 4b** and *cis*-Pt(COPh)(COMe)$(PPh_3)_2$.[1] Single crystals of **4b** suitable for X-ray diffraction were grown from C_6H_6/Et_2O. **For 4b**: IR ($CDCl_3$) ν_{CO} 2034, 1622 cm^{-1}; ^{31}P NMR ($CDCl_3$) δ 17.6 ($J_{P\text{-}Pt}$ = 1414 Hz); ^{1}H NMR ($CDCl_3$) δ 0.38 (3H, d, $J_{H\text{-}P}$ = 10.2 Hz, $J_{H\text{-}Pt}$ = 70.3 Hz, CH_3). **For 4b′**: ^{31}P NMR ($CDCl_3$) δ 21.7 ($J_{P\text{-}Pt}$ = 1963 Hz); ^{1}H NMR ($CDCl_3$) δ 0.95 (3H, d, $J_{H\text{-}P}$ = 6.2 Hz, $J_{H\text{-}Pt}$ ~ 74 Hz, CH_3).

SP-4-3-Pt(PPh_3)(CO)(COEt)(Et) (4c) and *SP*-4-4-Pt(PPh_3)(CO)(COEt)(Et) (4c′)

Complexes **4c** and **4c′** resulted from reaction of **3c** and CO in d_6-benzene and were identified by NMR techniques. **For 4c**: IR (C_6D_6) ν_{CO} 2050 cm^{-1}; ^{31}P NMR (C_6D_6) δ 16.2 ($J_{P\text{-}Pt}$ = 1257 Hz); ^{1}H NMR (C_6D_6) δ 1.18 (3H, t, $J_{H\text{-}H}$ = 7.4 Hz, CH_2CH_3), 1.33 (3H, t, $J_{H\text{-}H}$ = 7.4 Hz, $COCH_2CH_3$), 1.55 (2H, q, $J_{H\text{-}P}$ = 12.5 Hz, CH_2CH_3), 2.83 (2H, q, $J_{H\text{-}H}$ = 7.4 Hz, $COCH_2CH_3$). **For 4c′**: IR (C_6D_6) ν_{CO} 2075 cm^{-1}; ^{31}P NMR (C_6D_6) δ 18.2 ($J_{P\text{-}Pt}$ = 1762 Hz); ^{1}H NMR (C_6D_6) δ 0.89 (3H, t, $J_{H\text{-}H}$ = 7.3 Hz, $COCH_2CH_3$), 1.86 (3H, q, $J_{H\text{-}P}$ ~ 8 Hz, CH_2CH_3), 2.12 (2H, q, $J_{H\text{-}P}$ ~ 9 Hz, CH_2CH_3), δ 2.19 (2H, q, $J_{H\text{-}H}$ = 7.3 Hz, $COCH_2CH_3$).

cis-Pt(COEt)$_2$(PPh$_3$)$_2$ (5c)

^{31}P NMR (C_6D_6) δ 14.01 ($J_{P\text{-}Pt}$ = 1540 Hz); ^{1}H NMR (C_6D_6) δ 0.78 (6H, t, $J_{H\text{-}H}$ = 7.2 Hz, CH_3), 2.55 (4H, t, $J_{H\text{-}H}$ = 7.2 Hz, CH_2).

X-ray Crystallographic Analysis

Diffraction data were measured at on a Nonius CAD-4 diffractometer. Cell parameters were determined by a least-squares fit on 25 reflections. Intensity data were corrected for absorption on the basis of an experimental ψ rotation curve. The refinement proceeded was by a full-matrix least-squares method including all non-hydrogenic atoms anisotropically. Hydrogen atoms were fixed at the ideal geometry and the C-H distance 1.0 Å; their isotopic thermal parameters were fixed to values of attached carbon atoms at convergence of the isotropic refinement. Atomic scattering factors were taken from the International Tables of Crystallographic Data, Vol. IV. Computing programs were from the NRC VAX package.[11] Crystallographic data and selected bond parameters of **2b, 2c, 3b** and **4b** are listed in Tables 1, 2 and 3.

Table 1. X-ray Crystal Parameters and Data Collection for **2b, 2c, 3b** and **4b**

Compound	**2b**[a]	**2c**	**3b**	**4b**
formula	$C_{43.5}H_{38}P_2PtCl$	$C_{40}H_{40}P_2Pt$	$C_{44}H_{38}OP_2Pt$	$C_{27}H_{23}O_2PPt$
formula mass/g	853.26	777.79	839.83	605.55
cryst dimns/mm	0.2 × 0.5 × 0.6	0.30 × 0.35 × 0.45	0.4 × 0.5 × 0.6	0.15 × 0.4 × 0.6
space group	$C_{2/c}$	$C_{2/c}$	$P2_1/n$	$P\bar{1}$
a/Å	32.982 (5)	12.115 (3)	11.290 (2)	9.178 (1)
b/Å	10.727 (3)	17.294 (6)	17.857 (4)	10.305 (3)
c/Å	22.424 (4)	16.693 (6)	18.306 (4)	13.425 (3)
α/deg	90	90	90	106.91 (2)
β/deg	109.68 (2)	93.18 (3)	98.74 (2)	104.82 (3)
γ/deg	90	90	90	91.14 (2)
V/Å^3	7470	3420	3648	1146
Z	8	4	4	2
ρ,(calcd)/g cm^{-3}	1.517	1.480	1.529	1.697
F(000)	3399	1552	1728	840
Mo Kα, λ/Å	0.7107	0.7107	0.7107	0.7107
T, K	300	300	300	300
μ/mm^{-1}	3.98	3.97	4.01	6.38
transmission	0.45-1.0	0.65-1.0	0.80-1.0	0.56-1.0
2θ (max)/deg	50	50	45	50
h, k, l	(-39; 36), 12, 26	±14, 20, 19	±12, 19, 19	±10, 12, ±15
No of reflns measd	6571	3077	5031	4290
No of reflns obsd	4109 (> 2.0σ)	2750 (> 2.0σ)	3032 (> 1.5σ)	3444 (> 1.5σ)
No of variables	435	457	434	280
R(F)	0.055	0.022	0.048	0.030
R_w(F)	0.070	0.019	0.033	0.023
S	1.86	1.66	1.351	1.394
$(\Delta/\sigma)_{max}$	0.0722	0.0418	0.175	0.028

[a] disordered solvent packing

Table 2. Selected Bond Distances/Å and Angles/deg

trans-Pt(Me)(Ph)(PPh$_3$)$_2$ (**2b**)			
Pt-P1	2.271 (4)	C2-C7	1.42 (2)
Pt-P2	2.300 (4)	C3-C4	1.39 (2)
Pt-C1	2.13 (2)	C4-C5	1.40 (3)
Pt-C2	2.10 (2)	C5-C6	1.39 (3)
C2-C3	1.35 (2)	C6-C7	1.36 (3)
P1-Pt-P2	175.8 (2)	Pt-C2-C7	121 (1)
P1-Pt-C1	86.3 (5)	C3-C2-C7	118 (2)
P1-Pt-C2	92.9 (5)	C2-C3-C4	121 (2)
P2-Pt-C1	90.2 (5)	C3-C4-C5	120 (2)
P2-Pt-C2	90.5 (5)	C4-C5-C6	120 (2)
C1-Pt-C2	177.8 (6)	C5-C6-C7	118 (2)
Pt-C2-C3	122 (2)	C2-C7-C6	123 (2)
trans-Pt(Et)$_2$(PPh$_3$)$_2$ (**2c**)			
Pt-P	2.257 (1)	Pt-C1′	2.185 (3)
Pt-P′	2.257 (1)	C1-C2	1.420 (6)
Pt-C1	2.185 (3)	C1′-C2′	1.420 (6)
P-Pt-P′	178.18 (4)	P′-Pt-C1′	85.28 (9)
P-Pt-C1	85.28 (9)	C1-Pt-C1′	175.1 (2)
P-Pt-C1′	94.64 (9)	Pt-C1-C2	115.2 (3)
P′-Pt-C1	94.64 (9)	Pt-C1′-C2′	115.2 (3)
cis-Pt(COPh)(Me)(PPh$_3$)$_2$ (**3b**)			
Pt-P1	2.297 (3)	C71-C72	1.38 (2)
Pt-P2	2.338 (3)	C71-C76	1.39 (2)
Pt-C	2.179 (1)	C72-C73	1.37 (2)
Pt-C1	2.079 (1)	C73-C74	1.33 (3)
C1-O1	1.17 (2)	C74-C75	1.33 (3)
C1-C71	1.53 (2)	C75-C76	1.36 (2)
P1-Pt-P2	99.5 (1)	O-C1-C71	118 (1)
P1-Pt-C	173.0 (3)	C1-C71-C72	122 (1)
P1-Pt-C1	92.1 (4)	C72-C71-C76	117 (1)
P2-Pt-C	87.5 (3)	C71-C72-C73	121 (1)
P2-Pt-C1	168.4 (4)	C72-C73-C74	119 (2)
C-Pt-C1	80.9 (4)	C73-C74-C75	123 (1)
Pt-C1-O1	125.0 (9)	C74-C75-C76	118 (2)
Pt-C1-C71	117.4 (8)	C71-C76-C75	122 (2)
SP-4-3-Pt(PPh$_3$)(CO)(COPh)(Me) (**4b**)			
Pt-P	2.350 (2)	C1-C41	1.504 (9)
Pt-C1	2.064 (6)	C41-C42	1.389 (9)
Pt-C2	1.897 (7)	C42-C43	1.37 (1)
Pt-C3	2.108 (7)	C43-C44	1.37 (1)
C1-O1	1.221 (8)	C44-C45	1.36 (1)
C2-O2	1.118 (8)	C45-C46	1.40 (1)
P-Pt-C1	171.8 (2)	Pt-C1-C41	119.4 (4)
P-Pt-C2	97.1 (2)	C1-C41-C42	120.3 (6)
P-Pt-C3	90.1 (2)	C1-C41-C46	121.0 (5)
C1-Pt-C2	90.6 (3)	C42-C41-C46	118.7 (6)
C1-Pt-C3	82.4 (2)	C41-C42-C43	119.7 (7)
C2-Pt-C3	171.7 (3)	C42-C43-C44	121.2 (7)
Pt-C1-O1	122.4 (5)	C43-C44-C45	120.6 (7)
Pt-C2-O2	174.9 (6)	C44-C45-C46	119.1 (7)
O1-C1-C41	118.2 (5)	C41-C46-C45	120.6 (6)

Table 3. Non-hydrogen Atomic Coordinates and B$_{eq}$

trans-Pt(Me)(Ph)(PPh$_3$)$_2$ (**2b**)				
	x	y	z	Beq
Pt	0.382933(16)	0.24577(6)	0.232774(25)	2.665(23)
P1	0.40366(12)	0.1229(4)	0.32036(19)	3.03 (17)
P2	0.36277(12)	0.3827(4)	0.14896(18)	2.70(16)
C1	0.4289(5)	0.3771(16)	0.2876(8)	4.0(8)
C2	0.3361(5)	0.1176(15)	0.1809(8)	3.6(7)
C3	0.3462(6)	0.0199(16)	0.1507(9)	4.4(9)
C4	0.3151(5)	-0.0649(16)	0.1168(9)	4.5(9)
C5	0.2723(6)	-0.0488(18)	0.1129(9)	5.3(9)
C6	0.2607(6)	0.0519(21)	0.1430(11)	6.1(11)
C7	0.2924(4)	0.1323(15)	0.1759(7)	3.3(7)
C1A	0.4620(5)	0.1173(15)	0.3589(8)	3.7(7)
C2A	0.4871(7)	0.115(3)	0.3226(12)	9.0(17)
C3A	0.5324(6)	0.105(3)	0.3510(11)	7.7(15)
C4A	0.5522(6)	0.0992(25)	0.4124(11)	6.8(13)
C5A	0.5258(7)	0.112(3)	0.4495(12)	8.3(16)
C6A	0.4830(6)	0.120(3)	0.4252(10)	8.1(15)
C1B	0.3820(5)	0.1752(15)	0.3814(7)	3.4(7)
C2B	0.3672(5)	0.3002(16)	0.3792(8)	3.8(8)
C3B	0.3524(7)	0.3453(19)	0.4252(10)	5.5(10)
C4B	0.3530(6)	0.269(3)	0.4757(9)	6.4(12)
C5B	0.3671(6)	0.1456(23)	0.4780(9)	5.6(11)
C6B	0.3813(5)	0.1025(16)	0.4308(8)	3.8(8)
C1C	0.3907(5)	-0.0426(14)	0.3138(7)	3.0(7)
C2C	0.3465(6)	-0.0736(16)	0.2940(9)	4.6(9)
C3C	0.3338(5)	-0.2009(17)	0.2865(9)	4.3(8)
C4C	0.3646(9)	-0.2903(21)	0.2993(12)	8.2(16)
C5C	0.4066(8)	-0.2562(24)	0.3166(16)	10.5(20)
C6C	0.4201(7)	-0.1360(18)	0.3273(12)	6.6(13)
C1D	0.4007(4)	0.5099(14)	0.1538(7)	2.7(6)
C2D	0.3886(5)	0.6346(14)	0.1544(8)	3.9(8)
C3D	0.4216(7)	0.7224(18)	0.1591(12)	6.8(13)
C4D	0.4627(6)	0.6953(19)	0.1642(10)	5.7(10)
C5D	0.4727(6)	0.5721(19)	0.1622(9)	5.0(10)
C6D	0.4430(5)	0.4795(16)	0.1592(8)	3.9(8)
C1E	0.3502(4)	0.3238(14)	0.0680(6)	2.8(6)
C2E	0.3751(6)	0.3479(19)	0.0297(8)	4.9(10)
C3E	0.3637(7)	0.2956(23)	-0.0291(9)	6.5(12)
C4E	0.3281(7)	0.2190(18)	-0.0527(8)	5.8(11)
C5E	0.3041(7)	0.1933(24)	-0.0161(10)	6.9(12)
C6E	0.3150(5)	0.2431(19)	0.0441(7)	4.1(8)
C1F	0.3125(4)	0.4639(14)	0.1448(7)	2.7(6)
C2F	0.2887(6)	0.5280(17)	0.0899(9)	4.5(9)
C3F	0.2537(6)	0.5958(18)	0.0892(9)	4.9(9)
C4F	0.2392(5)	0.5991(19)	0.1399(9)	5.1(10)
C5F	0.2631(6)	0.5347(21)	0.1948(10)	5.9(11)
C6F	0.2978(5)	0.4646(15)	0.1967(8)	3.4(7)
C	1/2	1/2	0	22.2(31)
C11	0.5342(10)	0.408(4)	0.0014(15)	25.1(31)
C12	0.5413(6)	0.556(4)	0.0435(11)	26.1(27)
trans-Pt(Et)$_2$(PPh$_3$)$_2$ (**2c**)				
	x	y	z	Beq
Pt	0	0.340142(13)	1/4	2.261(8)
P	0.18365(7)	0.34222(6)	0.23366(5)	2.59(4)

C1	-0.0171(3)	0.34550(23)	0.11911(20)	3.10(17)
C2	-0.0536(3)	0.4177(3)	0.08699(22)	4.34(22)
C1A	0.2169(3)	0.42815(19)	0.17720(21)	2.67(16)
C2A	0.1840(3)	0.49851(21)	0.20878(23)	3.86(20)
C3A	0.2029(4)	0.56719(21)	0.17024(25)	4.54(23)
C4A	0.2532(4)	0.56611(21)	0.09833(25)	4.36(22)
C5A	0.2840(3)	0.49691(23)	0.06531(23)	4.27(21)
C6A	0.2656(3)	0.42783(21)	0.10441(22)	3.39(18)
C1B	0.2847(3)	0.34564(21)	0.31921(20)	2.71(16)
C2B	0.3595(3)	0.40458(22)	0.33387(24)	3.73(20)
C3B	0.4344(3)	0.4010(3)	0.3995(3)	4.98(22)
C4B	0.4356(3)	0.3393(3)	0.45029(24)	5.36(23)
C5B	0.3622(3)	0.27965(24)	0.43699(24)	4.49(21)
C6B	0.2870(3)	0.28285(21)	0.37191(22)	3.43(18)
C1C	0.2367(3)	0.25854(20)	0.18077(21)	2.92(18)
C2C	0.3482(3)	0.25031(22)	0.1682(3)	4.10(20)
C3C	0.3865(4)	0.18481(23)	0.1309(3)	5.25(23)
C4C	0.3139(4)	0.12750(23)	0.1069(3)	5.40(25)
C5C	0.2030(4)	0.13413(22)	0.1199(3)	5.10(23)
C6C	0.1642(3)	0.20011(21)	0.15694(23)	3.80(19)

cis-Pt(COPh)(Me)(PPh$_3$)$_2$ **(3b)**

	x	y	z	Biso
PT	0.21140(4)	0.12743(3)	0.16751(3)	2.740(23)
P1	0.0146(3)	0.16501(19)	0.14805(16)	2.82(15)
P2	0.2887(3)	0.20941(20)	0.08702(19)	3.31(16)
C	0.3914(10)	0.0814(8)	0.1949(7)	5.0(7)
C1	0.1793(11)	0.0496(7)	0.2432(6)	3.6(6)
O1	0.1640(9)	-0.0141(5)	0.2311(5)	5.8(6)
C11	-0.0714(10)	0.1374(7)	0.0611(6)	3.3(6)
C12	-0.1949(11)	0.1469(7)	0.0470(7)	4.3(7)
C13	-0.2616(11)	0.1242(9)	-0.0189(7)	5.3(7)
C14	-0.2037(14)	0.0914(8)	-0.0727(7)	6.6(9)
C15	-0.0840(14)	0.0792(7)	-0.0589(6)	5.3(9)
C16	-0.0171(12)	0.1022(7)	0.0082(6)	4.0(7)
C21	-0.0003(10)	0.2662(6)	0.1563(6)	2.8(6)
C22	-0.0772(10)	0.3087(7)	0.1064(6)	3.5(6)
C23	-0.0827(11)	0.3864(7)	0.1190(6)	4.4(7)
C24	-0.0143(13)	0.4197(7)	0.1765(7)	4.5(7)
C25	0.0638(11)	0.3769(8)	0.2244(6)	4.0(7)
C26	0.0706(11)	0.3020(7)	0.2150(6)	3.5(6)
C31	-0.0814(10)	0.1293(7)	0.2134(6)	3.3(6)
C32	-0.1144(13)	0.0553(8)	0.2088(7)	5.0(8)
C33	-0.1911(13)	0.0239(9)	0.2548(8)	6.7(9)
C34	-0.2271(14)	0.0711(9)	0.3073(8)	7.0(9)
C35	-0.1931(14)	0.1420(9)	0.3136(8)	6.9(9)
C36	-0.1226(13)	0.1716(7)	0.2661(7)	5.1(8)
C41	0.2055(11)	0.2847(7)	0.0382(7)	3.8(7)
C42	0.2153(11)	0.3600(8)	0.0569(7)	4.9(8)
C43	0.1494(14)	0.4151(8)	0.0151(8)	6.7(10)
C44	0.0664(13)	0.3949(8)	-0.0454(8)	6.6(9)
C45	0.0547(12)	0.3225(9)	-0.0668(7)	5.7(8)
C46	0.1218(12)	0.2682(7)	-0.0252(7)	4.5(7)
C51	0.3449(10)	0.1622(7)	0.0094(6)	3.1(6)
C52	0.3957(11)	0.2025(7)	-0.0427(7)	4.1(7)
C53	0.4307(11)	0.1642(8)	-0.1037(6)	4.9(8)
C54	0.4154(12)	0.0889(8)	-0.1102(7)	5.3(8)
C55	0.3661(13)	0.0494(8)	-0.0603(8)	6.1(9)
C56	0.3315(12)	0.0848(7)	0.0022(7)	4.6(7)
C61	0.4166(10)	0.2563(7)	0.1415(7)	3.5(6)
C62	0.5322(11)	0.2514(9)	0.1259(7)	5.4(9)
C63	0.6267(12)	0.2839(11)	0.1743(9)	8.2(11)
C64	0.6039(13)	0.3198(9)	0.2361(7)	6.5(9)
C65	0.4933(13)	0.3240(9)	0.2509(7)	6.2(9)
C66	0.3994(12)	0.2929(9)	0.2033(7)	5.8(9)
C71	0.1720(12)	0.0770(7)	0.3214(7)	4.7(7)
C72	0.2183(13)	0.1453(8)	0.3473(7)	5.9(9)
C73	0.2061(16)	0.1696(10)	0.4166(8)	8.6(11)
C74	0.1478(15)	0.1273(13)	0.4591(8)	10.8(13)
C75	0.1014(17)	0.0607(12)	0.4379(8)	10.4(14)
C76	0.1127(14)	0.0356(10)	0.3689(7)	7.4(11)
CHA	0.404	0.059	0.245	4.4
CHB	0.453	0.121	0.192	4.4
CHC	0.392	0.042	0.154	4.4

SP-4-3-Pt(PPh$_3$)(CO)(COPh)(Me) **(4b)**

	x	y	z	Biso
PT	0.07441(3)	0.462253(24)	0.242884(20)	2.455(11)
P	0.05123(18)	0.68038(15)	0.35124(13)	2.44(7)
C11	-0.1470(7)	0.7156(6)	0.3328(5)	2.7(3)
C12	-0.2473(7)	0.6154(6)	0.3391(5)	3.4(4)
C13	-0.3995(8)	0.6397(8)	0.3300(6)	4.6(4)
C14	-0.4506(8)	0.7588(8)	0.3143(6)	4.7(4)
C15	-0.3523(8)	0.8541(7)	0.3077(6)	4.4(4)
C16	-0.2009(7)	0.8336(6)	0.3178(5)	3.4(3)
C21	0.1386(7)	0.7233(5)	0.5011(5)	2.6(3)
C22	0.0571(8)	0.7682(6)	0.5720(5)	3.6(3)
C23	0.1251(9)	0.7964(7)	0.6844(6)	4.6(4)
C24	0.2773(10)	0.7788(7)	0.7259(5)	4.7(5)
C25	0.3626(8)	0.7362(6)	0.6569(6)	4.4(4)
C26	0.2953(8)	0.7074(6)	0.5446(5)	3.4(3)
C31	0.1385(7)	0.8159(6)	0.3189(5)	2.6(3)
C32	0.1233(8)	0.7977(6)	0.2088(5)	3.9(4)
C33	0.1866(9)	0.9003(7)	0.1812(5)	4.6(4)
C34	0.2674(8)	1.0166(7)	0.2614(6)	4.5(4)
C35	0.2839(9)	1.0327(6)	0.3695(6)	4.6(4)
C36	0.2197(8)	0.9342(6)	0.3985(5)	3.8(4)
C1	0.0788(7)	0.2797(6)	0.1285(5)	3.2(3)
O1	-0.0179(6)	0.1812(4)	0.0999(4)	4.5(3)
C41	0.2068(7)	0.2653(6)	0.0798(5)	2.9(3)
C42	0.2203(8)	0.1397(7)	0.0108(5)	4.2(4)
C43	0.3396(10)	0.1271(8)	-0.0309(6)	5.7(5)
C44	0.4455(10)	0.2367(10)	-0.0070(6)	5.9(6)
C45	0.4341(8)	0.3614(8)	0.0583(6)	5.0(5)
C46	0.3142(8)	0.3763(6)	0.1030(5)	3.4(4)
C2	0.2355(8)	0.4205(6)	0.3534(5)	3.8(4)
O2	0.3257(6)	0.3863(5)	0.4151(4)	6.3(3)
C3	-0.1151(8)	0.4778(7)	0.1109(5)	4.4(4)

ACKNOWLEDGMENT

We thank the National Science Council, Taipei, Taiwan, ROC for financial support.

Supplementary materials

Fully labeled ORTEP drawings, tables of complete crystal data, atomic coordinates, bond lengths and bond angles, and thermal parameters for complexes **2b, 2c, 3b**, and **4b** (7 pages) will be available from JTC.

Received July 11, 1994.

Key Words

Diorganoplatinum; Carbonylation; Dialkyl complexes; Acyl alkyl complexes.

REFERENCES

1. Part 1: Chen, J.-T.; Yeh, Y.-S.; Yang, C.-S.; Tsai, F.-Y.; Huang, G.-L.; Shu, B.-C.; Huang, T.-M.; Chen, Y.-S.; Lee, G.-H.; Cheng, M.-C.; Wang, C.-C.; Wang, Y. *Organometallics* **1994**, *13* (in press).
2. For general review: (a) "*Comprehensive Coordination Chemistry*" Wilkinson, G. FRS, Ed.; Pergamon Press Ltd.: Elmsford, New York, 1982; Vol. 6, 8. (b) "*Comprehensive Organometallic Chemistry*" Wilkinson, G. FRS, Ed.; Pergamon Press Ltd.: Elmsford, New York, 1982; Vol. 6, 8. (c) Hartley, F. R. "*The Chemistry of Platinum and Palladium*" Applied Science, London, 1973. (d) Heck, R. F. "*Organo-transition Metal Chemistry*", Academic Press, New York, N. Y., 1974. (e) Colquhoun, H. M.; Thompson, D. J.; Twigg, M. V. "*Carbonylation: Direct Synthesis of Carbonyl Compounds*", Plenum Press. New York, N. Y., 1991.
3. Chatt, J.; Shaw, B. L. *J. Chem. Soc.* **1959**, 705 and 4020.
4. (a) Booth, G.; Chatt, J. *J. Chem. Soc. A.* **1966**, 634. (b) Anderson, G. K.; Clark, H. C.; Davis, J. A. *Inorg. Chem.* **1981**, *20*, 3607.
5. Ozawa, F.; Yamamoto, A. *Chem. Lett.* **1981**, 289.
6. (a) Coulson, D. R. *J. Am. Chem. Soc.* **1976**, *98*, 3111. (b) Kim, Y.-J.; Osakada, K.; Takenaka, A.; Yamamoto, A. *J. Am. Chem. Soc.* **1990**, *112*, 1096.
7. Chen, J.-T.; Huang, T.-M.; Cheng, M.-C.; Wang, Y. *Organometallics* **1990**, *9*, 539.
8. Furlani, A.; Licoccia, S.; Russo, M. *J. Chem. Soc. Dalton Trans.* **1982**, 2449.
9. Appleton, T. G.; Bennett, M. A. *Inorg. Chem.* **1978**, *17*, 738.
10. (a) Wojcicki, A. *Adv. Organomet. Chem.* **1973**, *11*, 88. (b) Anderson, G. K.; Cross, R. J. *J. Chem. Soc., Dalton Trans.* **1979**, 1246.
11. NRC VAX: Gabe, E. J.; LePage, Y.; Charland, J.-P.; Lee, F. L.; White, P. S. *J. Appl. Cryst.* **1989**, 22, 384.