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Chemistry of α-Ketoacyl Metal Complexes†

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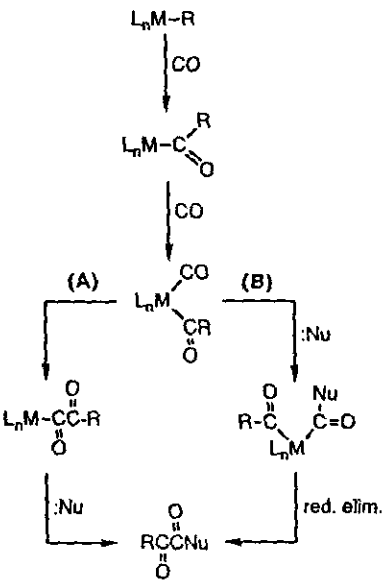
The α-ketoacyl complexes constitute a new family of organometallic compounds. The α-ketoacyl ligands have a strong influence and generally follow a decreasing order of acyl > α-ketoacyl > alkyl or aryl. The oxalyl conformation exhibits planar *s*-cis, perpendicular and planar *s*-trans structures. In comparison with the standard $C(sp^2)$-$C(sp^2)$ bond, the oxalyl C-C bonds of the α-ketoacyl ligands are relatively long, indicating that the electronic delocalization between the oxalyl carbonyls are of the least importance. The weak C-C bond between the α-ketoacyl carbonyls affords a driving force of the decarbonylative reactivity of such ligands; it is also responsible for the difficulty of formation of the α-ketoacyl complex via insertion of CO into the metal-acyl bond. However, α-ketoacyl complexes can be kinetically stable. Kinetic studies of decarbonylation of the α-ketoacyl complexes provided a profound understanding of the mechanism of novel catalytic reactions of double carbonylation. The α-ketoacyl complexes show promise to explore rare acyl migration and the reductive coupling of $C(sp^2)$-$C(sp^2)$ bonds in a fundamental way.

INTRODUCTION

The α-ketoacyl metal complexes L_nM-C(O)C(O)R have been of interest mainly because of the possibility of involvement of these species in catalytic reactions of double-carbonylation.[1] From a mechanistic point of view (Scheme I), a metal-acyl species could be first formed through migratory insertion of CO from a metal-alkyl (or metal-aryl) species. The ensuing coordination of CO would result in an acyl carbonyl complex which might either undergo a successive insertion of CO via intermediacy of an α-ketoacyl complex (path A) or suffer nucleophilic attack at the CO ligand to give a "diacyl" complex (path B), eventually transforming to organic doubly carbonylated products. These complexes have the intrinsic novelty of rare α-ketoacyl ligands and the potential use of such species to probe the feasibility of relatively unexplored migratory insertion of CO into a metal-acyl bond.[2] The development of chemistry of diorgano derivatives containing α-ketoacyl ligands, specifically in the systems of square-planar group 10 metals, further affords the opportunity for mechanistic studies on reactions of carbonylation and decarbonylation.[3] In this account, we summarize recent investigation and understanding in the chemistry of the title complexes.

Scheme I



SYNTHESES

The most convenient known procedures to prepare α-ketoacyl complexes involve conventional nucleophilic addition or oxidative addition of an α-ketoacyl halide to a reductive metal center.[4] The first instance of such a reaction was the nucleophilic addition of pyruvoyl chloride to

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This review is invited to commemorate the sixtieth anniversary of the Chinese Chemical Society.
Dedicated to Professor Zui-Feng Lin (林瑞樅教授), my first mentor of chemistry, on his retirement from the Department of Chemistry, National Taiwan University.
† Partially based on the Ph.D. thesis of Yu-Sung Yeh, National Taiwan University, 1992.

$NaMn(CO)_5$, leading to a pyruvoylcarbonylmanganese compound $Mn(COCOMe)(CO)_5$.[5] Similarly, α-ketoacyl complexes of Fe, Mo[6] and Re[7] have been obtained (Eq. 1). Oxidative addition of RCOCOCl to d^{10} group-10 metal complexes resulted in the formation of four-coordinate halo(α-ketoacyl) products (Eq. 2).[8] Analogous reaction of the Vaska complex $Ir(CO)Cl(PPh_3)_2$, yielding six-coordinate $Ir(COCOR)(PPh_3)_2(CO)Cl_2$ was also achieved.[9]

$$\begin{aligned}&RCOCOX + Na[M(CO)_xL_n] \longrightarrow \\ &\quad RC(O)C(O)M(CO)_xL_n + NaX \qquad (1)\\ &\quad (X = \text{halide}; L = CO, Cp)\end{aligned}$$

$$\begin{aligned}&RCOCOX + ML_4 \text{ or } ML_2(\text{olefin}) \longrightarrow \\ &\quad trans\text{-}M(COCOR)(X)L_2 + 2L\ (\text{olefin}) \qquad (2)\\ &\quad (M = Pd, Pt; X = \text{halide}; L = PR'_3)\end{aligned}$$

Although there has been evidence that metal-mediated consecutive insertion of CO is kinetically disfavored,[2b,10] formation of the α-ketoacyl complex via insertion of CO into a metal-acyl bond has been observed in some highly energized systems. This chemistry was first found to occur in 17-electron species of group-7 metals in which the carbonylation was promoted by the addition of NO (Eqs. 3 and 4).[11] Another example is the incorporation of acetylene into an "A-frame" diruthenium complex along with two carbonyls to form a five-membered α-ketoacyl metallacycle (Eq. 5). This appears to have been formed by the insertion of two carbonyl ligands into a metal-alkyne bond.[12] In these cases, the energized metal-acyl species presumably provide the driving force for the difficult carbonylation. Besides the d-block metals, a few f-block metal complexes exhibit the ability to adopt CO successively to form vicinal carbonyl moieties.[13] The oxyphilicity of the f-block elements is considered to be crucial to the formation of oxycarbene-like η^2-acyl which may facilitate the coupling with carbon monoxide.

$$\begin{aligned}&CpM(COR)(CO)_2 + NO \longrightarrow \\ &\quad CpM(COCOR)(CO)(NO)\quad (M = Mn, Re) \qquad (3)\end{aligned}$$

$$\begin{aligned}&CpFe(COR)(CO)(PPh_3)^+ + NO \longrightarrow \\ &\quad CpFe(COCOR)(NO)(PPh_3)^+ \qquad (4)\end{aligned}$$

$$\begin{aligned}&Ru_2(CO)_4(\mu\text{-dmpm})_2(\mu\text{-CO}) + 2\,E\text{-}C{\equiv}C\text{-}E \longrightarrow \\ &\quad Ru_2(\mu\text{-dmpm})_2(CO)_3(\mu\text{-}C_2E_2)(COCOC_2E_2)\\ &\quad + 2\,CO \qquad (5)\end{aligned}$$

The halo complexes are particularly advantageous for preparing other α-ketoacyl derivatives. The derivation has been mainly demonstrated by the halo(α-ketoacyl) platinum(II) complexes trans-$Pt(COCOR)(X)L_2$. The displacement of halide ligand readily resulted from the assistance of silver reagents. When $AgOSO_2CF_3$ or AgSCN is employed, the reaction of transmetallation takes place (Eq. 6).[14] While non-coordinating tetrafluoroborate salt is being used, addition of the replacing ligands is necessary to prevent decomposition of the α- ketoacyl complexes, and leads to various substituted cationic products (Eq. 7). The carbonyl derivatives trans-$[Pt(COCOR)(CO)(PPh_3)_2](BF_4)$ undergo nucleophilic addition of alcohol or amine at the carbon atom of the terminal CO to yield complexes of the "diacyl" type (Eq. 8).[15]

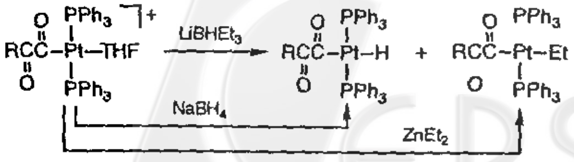
$$\begin{aligned}&trans\text{-}Pt(COCOR)(Cl)(PPh_3)_2 + Ag^+(Nu^-) \longrightarrow \\ &\quad trans\text{-}Pt(COCOR)(Nu)(PPh_3)_2 + AgCl \qquad (6)\\ &\quad (Nu = OTf, SCN)\end{aligned}$$

$$\begin{aligned}&trans\text{-}Pt(COCOR)(Cl)(PPh_3)_2 + AgBF_4 + L \longrightarrow \\ &\quad trans\text{-}[Pt(COCOR)(L)(PPh_3)_2](BF_4) + AgCl \qquad (7)\\ &\quad (L = THF, Me_2CO, MeCN, H_2O, C_2H_4,\\ &\quad CO, PPh_3)\end{aligned}$$

$$\begin{aligned}&trans\text{-}[Pt(COCOR)(CO)(PPh_3)_2](BF_4) + E^+Nu^- \\ &\quad \longrightarrow trans\text{-}Pt(COCOR)(CONu)(PPh_3)_2\\ &\quad + E^+BF_4^- \qquad (8)\\ &\quad (Nu = OR', NR'_2; E = Li, Na, H)\end{aligned}$$

Transmetallation of halo(α-ketoacyl)platinum(II) complexes with diorganozinc reagents affords an convenient synthetic route to the alkyl (or aryl) α-ketoacyl complexes (Eq. 9). Similar reactions of trans-$Pt(COCOR)(OTf)(PPh_3)_2$ or trans-$[Pt(COCOR)(H_2O)(PPh_3)_2](BF_4)$ with diorganozincs lead to the same products.[16] The reactions of trans-$[Pt(COCOR)(THF)(PPh_3)_2](BF_4)$ with $NaBH_4$ yield hydrido(α-ketoacyl) derivatives. The replacement of super hydride reagent $LiBHEt_3$ for $NaBH_4$ results in both hydrido and ethyl products together, but in relatively poor yields (Scheme II).[17] Acetylide derivatives are prepared from the reaction of the halo complex and acetylene promoted by amine (Eq. 10).[14]

Scheme II



$$\textit{trans}\text{-}\mathrm{Pt(COCOR)(Cl)(PPh_3)_2} + 1/2\,\mathrm{ZnR'_2} \longrightarrow \textit{trans}\text{-}\mathrm{Pt(COCOR)(R')(PPh_3)_2} + \mathrm{R'ZnCl} \qquad (9)$$

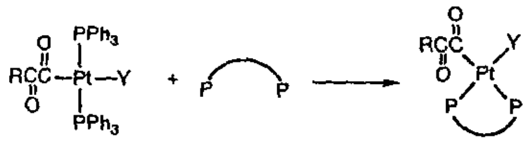
$$\textit{trans}\text{-}\mathrm{Pt(COCOR)(Cl)(PPh_3)_2} + \mathrm{R'C{\equiv}CH} + \mathrm{R''_3N} \longrightarrow \textit{trans}\text{-}\mathrm{Pt(COCOR)(C{\equiv}CR')(PPh_3)_2} + \mathrm{R''_3NHCl} \qquad (10)$$

The trans alkyl (or aryl) α-ketoacyl complexes undergo facile carbonylation to form selectively cis acyl α-ketoacyl complexes (Eq. 11).[16] Isomerization of *trans*-$\mathrm{Pt(COCOR)(CONR'_2)(PPh_3)_2}$ to the cis derivative is induced by addition of amine in the presence of CO.[18]

$$\textit{trans}\text{-}\mathrm{Pt(COCOR)(R')(PPh_3)_2} + \mathrm{CO} \longrightarrow \textit{cis}\text{-}\mathrm{Pt(COCOR)(COR')(PPh_3)_2} \qquad (11)$$

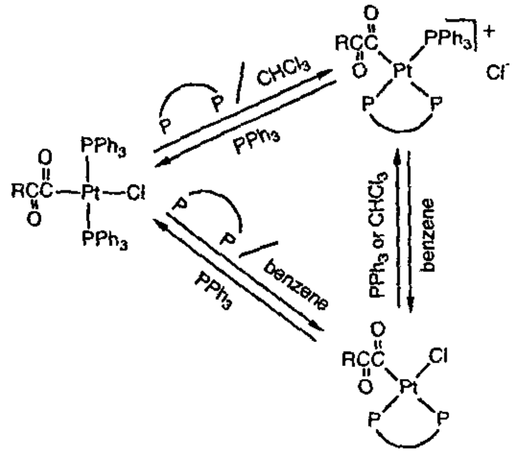
Direct substitution of the bidentate ligand for the monodentates in the trans species also leads to the cis complexes (Scheme III). The substitution reactions of halo complexes by dppe (diphenylphosphinoethane) result in ionic products in polar solvents, but neutral products in nonpolar environment (Scheme IV).[19]

Scheme III



(Y = alkyl, aryl, COOR', CONR'₂)

Scheme IV



CHARACTERIZATION AND STRUCTURES

The infrared and ^{13}C NMR spectra of the α-ketoacyl complexes are characteristic. There are generally two strong well-resolved IR absorption lines in the region 1600-1750 cm^{-1} which are associated with the stretching modes of oxalyl carbonyls. The line of smaller wavenumber is due to the carbonyl group adjacent to the metal. The vibrational wavenumber of the α-carbonyl of trans alkyl α-ketoacyl complex *trans*-$\mathrm{Pt(COCOR)(R')(PPh_3)_2}$ is relatively small (usually < 1600 cm^{-1}). The reason may be the good electron-releasing ability of the alkyl group which enhances π back-donation to the α-ketoacyl ligand, and weakens the α-C-O bond. In the ^{13}C NMR spectra, two carbonyl resonances provide sound evidence for the α-ketoacyl ligands. The line due to the metal-bound carbonyl carbon appears at larger δ than that of the β-carbon, and shows large $J_{\text{C-Pt}}$ value (Table 1).

The magnitude of a coupling constant such as $^1J_{\text{P-Pt}}$ is assumed generally to be dominated by the Fermi contact term, and is useful for estimating the trans influence of ligands experimentally.[20] Bennett et al have measured values of $^1J_{\text{P-Pt}}$ for compounds $\mathrm{Pt(CH_3)(L)(dppe)}$ in which L represents a carbon σ-donor ligand. The results indicate that the acyl, alkyl and aryl groups are all in the category of strong trans influence, the acyl ligands generally showed greater influence than the latter, the order being $\mathrm{-C(O)C_6H_9 > C_6H_9 \sim Et > Ph > -CH_2Ph \sim Me}$.[21,22] The measurments of $^1J_{\text{P-Pt}}$ for *cis*-$\mathrm{Pt(COCOR)(COR')(PPh_3)_2}$ and $\mathrm{[Pt(PPh_3)(dppe)(L)](X)}$ (L = α-ketoacyl or other carbon σ-donor ligand; X = halide or $\mathrm{BF_4}$) allow one to conclude that the trans influence of the α-ketoacyl ligand falls roughly between those of acyl and alkyl ligands. The extended list is: $\mathrm{-C(O)Et > -C(O)Me > -C(O)Ph > Et \sim -COCOPh, -COCOEt, -COCOMe > Ph > -COCOOMe > -COOMe > -CH_2Ph > Me}$.[16]

A distinctive feature of the α-ketoacyl complexes is that many trans derivatives are highly colored. For instance, in contrast to most colorless or yellow organoplatinum(II) complexes, striking colors such as pink for *trans*-$\mathrm{Pt(COCOR)(Cl)(PPh_3)_2}$, turquoise for *trans*-$\mathrm{Pt(COCOR)(CONR'_2)(PPh_3)_2}$, violet for *trans*-$\mathrm{Pt(COCOR)(COOR)(PPh_3)_2}$, purple for *trans*-$\mathrm{Pt(COCOR)(R')(PPh_3)_2}$ and *trans*-$\mathrm{Pt(COCOR)(H)(PPh_3)_2}$ (R = Me, Et, Ph) have been obtained. The more electron-withdrawing α-ketoacyl ligand, in comparison with the acyl ligand, would be expected to have lower energy of MLCT transition. Indeed, the electronic spectrum of the α-ketoacyl complex generally exhibits a long-

Table 1. Spectral Data of Selected α-Ketoacyl Complexes in the Form of *trans*-$Pt(COCOR)(X)(PPh_3)_2$ and *trans*-$Pt(COR)(X)(PPh_3)_2$[16]

	UV-VIS λ_{max}/nm (ε/cm^{-1}M^{-1})	IR νCO/cm^{-1}	^{13}C NMR α-CO/δ ($J_{C\text{-}Pt}$, $J_{C\text{-}P}$/Hz) β-CO/δ ($J_{C\text{-}Pt}$, $J_{C\text{-}P}$Hz)
trans-$Pt(COCOR)(X)(PPh_3)_2$			
X = Cl			
R = Et	456 (63)	1705, 1650	214.8 (1075, 6.9) 202.2 (179, 3.8)
Me	452 (57)	1699, 1638	214.4 (1084, 6.9) 200.5 (187, 4.1)
Ph	484 (67)	1659, 1637	216.0 (1100, 6.7) 200.5 (191, 4.3)
OMe	378 (90)	1726, 1708 (sh), 1654	208.2 (1142, 6.8) 163.8 (239, 5.0)
X = Et			
R = Et	554 (73)	1696, 1604	
Me	548 (57)	1693, 1590	
Ph	562 (87)	1653, 1560	
OMe	452 (89)	1710, 1596	
X = Me			
R = Me		1705, 1615	237.1 (844, unresolved) 168.7 (129, unresolved) -8.6 (398, 9.1, $PtCH_3$)
trans-$Pt(COR)(X)(PPh_3)_2$			
X = Br			
R = Me		1654	218.9 (930±10, 4.9) 43.6 (207, 6.1, CH_3)
X = Cl			
R = Ph		1611	212.5 (989, 6.1) 146.1 (159, 4.3, Cβ)
R = OMe		1656s, 1637w	168.9 (1334, 7.9) 50.3 ($J_{C\text{-}Pt}$ = 17.7, OCH_3)

wavelength band with absorption maxima mostly appearing in the region 450-550 nm which is about 200 nm greater than the corresponding band of the acyl analogue.

The methoxyoxalyl complexes are distinct from other α-ketoacyl complexes in several respects. As shown in Table 1, the IR absorptions of the β-CO in *trans*-$Pt(COCOOMe)(X)(PPh_3)_2$ (X = Cl, alkyl, aryl) are at higher wavenumbers than others. ^{13}C NMR data of the methoxyoxalyl carbonyls, particularly, β-CO contain significantly smaller chemical shifts than those of the analogues, and have stronger Pt-C coupling. The MLCT bands of methoxyoxalyl derivatives show a blue shift ca. 100 nm relative to other α-ketoacyl analogues, presumably due to the strongly electron-releasing -C(O)OMe group.

X-ray structures of single-crystals of α-ketoacyl complexes demonstrate three features of the oxalyl moiety: planar *s*-trans (with the largest torsional angle of O-C-C-O being 178°),[16] planar *s*-cis (the smallest angle, 10°),[15b] and perpendicular (the closest one, 102°)[11]. The distance of the oxalyl C-C bond is generally in the region 1.52-1.58 Å which is greater than the standard C(sp^2)-C(sp^2) bond. The crystallographic analysis indicates that electronic delocalization in α-ketoacyl ligands is of limited importance, and the broad span of the α-ketoacyl conformation may be influenced by steric or environmental conditions. The evidence is *trans*-$Pt(COCOPh)(Cl)(PPh_3)_2$ that showed two solid-state structures; in one, positional disorder existed for the two carbon atoms of the planar *s*-trans oxalyl groups (O-C-C-O torsional angle, 177°) because of a 180° rotation about the twofold axis through the Pt-Cl bond.[8c] In the other crystal containing benzene molecules packed in the lattice, the oxalyl moiety has an O-C-C-O torsional angle 131°.[23]

C(O)-C(O) BOND CLEAVAGE AND ACYL MIGRATION

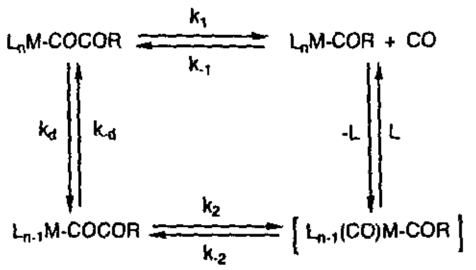
A representative reaction of α-ketoacyl complexes is that α-ketoacyl ligands undergo decarbonylation, transforming to acyl groups (Eq. 12). Although decarbonylation of the α-ketoacyl ligand resembles the intensively studied decarbonylation of the acyl ligand (Eq. 13), the former reaction consisting of rare acyl migration is kinetically and thermodynamically intriguing. α-Ketoacyl complexes

$$L_nM\text{-}C(O)C(O)R \longrightarrow L_n(CO)M\text{-}C(O)R \qquad (12)$$

$$L_nM\text{-}C(O)R \longrightarrow \Lambda_n(CO)M\text{-}R \qquad (13)$$

generally possess high kinetic stability. Two mechanisms of decarbonylation of α-ketoacyl complexes are that acyl migration initiates concurrent loss of another ligand (route k_1 in Scheme V), and that loss of a ligand might produce a coordinatively unsaturated intermediate which subsequently prompts acyl migration (route k_d & k_2 in Scheme V).[8c,10,24]

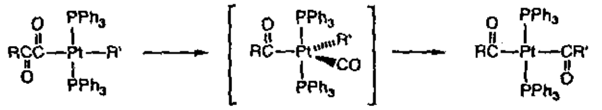
Scheme V



In decarbonylation of $Mn(COCOMe)(CO)_5$, the activation energy for dissociation of CO was determined to be 112.1 kJ/mol which is 12.7 kJ/mol greater than for the corresponding reaction of $Mn(COMe)(CO)_5$. Attempts to equilibriate the pyruvoyl and acetyl species led to predominant conversion of the pyruvoyl complex to the acetyl complex even under CO at 11 MPa. Hence the activation energy for carbonylation of $Mn(CO)_5(COMe)$, yielding $Mn(CO)_5(COCOMe)$, is estimated to be at least 42.2 kJ/mol above the barrier for insertion of CO into $Mn(CO)_5(Me)$. Carbonylative acyl migration is therefore a highly unlikely route in the substitution reactions of acyl metal complexes. Detailed kinetic studies of decarbonylation of square-planar complex *trans*-$Pd(COCOPh)(Cl)(PPh_3)_2$ are consistent with this conclusion. The rate of decarbonylation of the benzoylformyl complex of Pd(II) was unaffected at 25 °C by the presence of CO up to 4.7 MPa. Similarly, no trace of the benzoylformyl product was detected when *trans*-$Pd(COPh)(Cl)(PPh_3)_2$ was exposed to CO at 6.7 MPa and 25 °C. The least activation energy of carbonylation from a benzoyl complex of Pd(II) to the benzoylformyl product has been estimated as >> 116.3 kJ/mol. Decarbonylative acyl migration in a three-coordinate 14-electron Pd(II) center is about 16.7 kJ/mol lower than in a coordinatively saturated 16-electron center. Unlike *trans*-$Pd(COCOPh)(Cl)(PPh_3)_2$ that is prone to decarbonylation, decomposition of the platinum(II) analogue is negligible at 25 °C. Indeed, the activation energy for acyl migration in the chloro bezoylformyl complex of Pt(II) was found to be 21 kJ/mol greater than for the palladium complex.

Weakly solvated α-ketoacyl complexes and α-ketoacyl complexes containing labile ligands are kinetically unstable. For instance, cationic complexes *trans*-$[Pt(COCOPh)(L)(PPh_3)_2]^+$ (L = H_2O, THF, MeCN, acetone, CO, PPh_3 etc.), unlike *trans*-$Pt(COCOPh)(Cl)(PPh_3)_2$, suffer spontaneous decarbonylation to give *trans*-$[Pt(COPh)(CO)(PPh_3)_2]^+$ in solutions at 25 °C. Decarbonylation of neutral species such as *trans*-$Pt(COCOR)(Y)(PPh_3)_2$ (Y = OSO_2CF_3, H, CO_2R', $CONR'_2$ etc.) was observed, but were too complicated to be systematically examined. The alkyl (or aryl) α-ketoacyl complexes *trans*-$Pt(COCOR)(R')(PPh_3)_2$ spontaneously transform to *trans*-$Pt(COR)(COR')(PPh_3)_2$;[17] this reaction presumably occurs via an intramolecular transfer of CO, which may be initiated by decarbonylative acyl migration from the α-ketoacyl ligand to form a five-coordinate intermediate. The intermediate then undergoes a subsequent migratory insertion of CO to accomplish the diacyl product (Scheme VI).

Scheme VI



DOUBLE CARBONYLATON AND ACYL-ACYL COUPLING

Yamamoto and Tanaka have independently reported palladium-catalyzed formation of doubly carbonylated products through the reaction of organic halides with nucleophiles, such as amine, alcohol or water, in the presence of CO (Eq. 14). Carbonylative coupling of organic halides with organometals, leading to the formation of diketones, was also discovered (Eq. 15).[25] The kinetic investigation

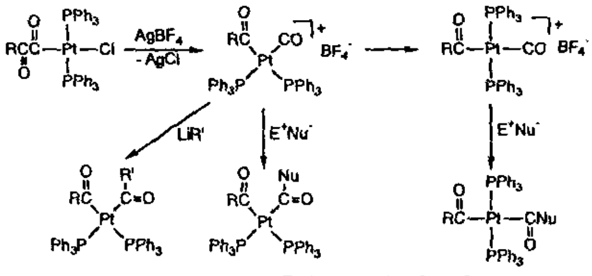
$$\begin{aligned}&RX + 2\,CO + NuH \xrightarrow{\text{"Pd(II)"}} \\ &\quad RC(O)C(O)Nu + HX \qquad (14) \\ &\quad (R = \text{aryl}; Nu = OR', NR'_2, OH)\end{aligned}$$

$$\begin{aligned}&RX + 2\,CO + MR'_n \xrightarrow{\text{"Pd(II)"}} \\ &\quad RC(O)C(O)R' + R'_{n-1}MX \qquad (15) \\ &\quad (M = Zn, Sn, Cd, Mg\ \text{etc.})\end{aligned}$$

of double carbonylation indicates that reductive elimination of two adjacent acyl groups in a "diacyl" intermediate is likely responsible for the formation of the C-C bond between two vicinal carbonyls. However, well characterized diacyl complexes and the study of acyl-acyl coupling are scarce.[26] The α-ketoacyl complexes of Pt(II) have provided convenient pathway to prepare good models of diacyl species for close examination on such subjects.

Removal of chloride from *trans*-Pt(COCOR)(Cl)-$(PPh_3)_2$ by treatment with silver(I) ion promotes decarbonylation of the α-ketoacyl ligand to form first a metastable cation *cis*-$[Pt(COR)(CO)(PPh_3)_2]^+$ which spontaneously isomerizes to the thermodynamically stable trans isomer. Both cis and trans acyl carbonyl complexes are subject to nucleophilic attack by alkoxide or amide to yield acyl alkoxycarbonyl and acyl carbamoyl complexes respectively (Scheme VII). The reaction of *cis*-$[Pt(COR)(CO)(PPh_3)_2]^+$ with organolithium gives a prototypical diacyl complex *cis*-$Pt(COR)(COR')(PPh_3)_2$.[27] Attempt to prepare a prototypical trans diacyl complex by nucleophilic addition has not yet been successful.

Scheme VII



E = H, Li, Na; Nu = OR', NR'$_2$

Thermal decomposition of *cis*-$Pt(COPh)(CONEt_2)(PPh_3)_2$ undergoes acyl-acyl coupling to yield α-keto amide $PhC(O)C(O)NEt_2$ as the major organic product.[28] The NMR spectrum of the benzoyl carbamoyl complex indicates that four methylene hydrogens in the carbamoyl ligand are diastereotopic, with hindered rotation of the carbamoyl group; the reason may be the uncommonly small angle, ∠C-Pt-C' = 79.6°, between the acyl and carbamoyl ligands. Another noticeable feature of this complex is the distinctive distance (only 2.63 Å) between the two carbonyl carbon atoms; the ground-state steric effect is probably crucial to the feasibility of the acyl-carbamoyl coupling.

RC(O)C(O)R' and RC(O)R' are elicited as products via acyl-acyl coupling from either *cis*-$Pt(COR)(COR')(PPh_3)_2$ or *cis*-$Pt(COCOR)(COR')(PPh_3)_2$,[16] but no formation of triketone has yet been detected. Apparently, reductive elimination of two acyl ligands (or acyl and α-ketoacyl ligands) competes with decarbonylation of acyl or α-ketoacyl groups. The rate of C-C coupling generally decreases in the order of acyl-alkyl ~ vinyl-alkyl > alkyl-alkyl.[29] Collman et al suggested that reductive coupling products likely form transient σ-complexes. The barrier to reductive elimination is thus influenced by the stability of the product complexes.[4] Accordingly, oxalyls containing a weak C-C bond are supposed to be disfavorably derived from acyl-acyl coupling. The development of the chemistry of α-ketoacyl and diacyl complexes has enabled advance of understanding of metal-mediated C-C bond formation.

CONCLUDING REMARKS

The α-ketoacyl complexes constitute a new family of organometallic compounds. The α-ketoacyl ligands have a strong influence and generally follow a decreasing order of acyl > α-ketoacyl > alkyl or aryl. The oxalyl conformation exhibits planar *s*-cis, perpendicular and planar *s*-trans structures. The oxalyl C-C bonds of the α-ketoacyl ligands are rather long, indicating that the electronic delocalization between the oxalyl carbonyls are of the least importance. The weak C-C bond between the α-ketoacyl carbonyls affords a driving force of the decarbonylative reactivity of such ligands; it is also responsible for the difficulty of formation of the α-ketoacyl complex via insertion of CO into the metal-acyl bond. However, α-ketoacyl complexes can be kinetically stable. Kinetic studies of decarbonylation of the α-ketoacyl complexes provided a profound understanding of the mechanism of novel catalytic reactions of double-carbonylation. The α-ketoacyl complexes show promise to explore rare acyl migration and the reductive coupling of $C(sp^2)$-$C(sp^2)$ bonds in a fundamental way.

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Key Words

α-Ketoacyl; Carbonylation; Decarbonylation; Double carbonylation; Acyl migration; Acyl-acyl coupling.

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