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Synthesis and application of diphenylbis(3,5-dimethylpyrazol-1-yl)methane to form η^2 -arene complexes of molybdenum

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Abstract

The neutral nitrogen-bidentate ligand, diphenylbis(3,5-dimethylpyrazol-1-yl)methane, $\text{Ph}_2\text{CPz}'_2$, can readily be obtained by the reaction of Ph_2CCl_2 with excess HPz' in a mixed-solvent system of toluene and triethylamine. It reacts with $[\text{Mo}(\text{CO})_6]$ in 1,2-dimethoxyethane to give the η^2 -arene complex, $[\text{Mo}(\text{Ph}_2\text{CPz}'_2)(\text{CO})_3]$ (1). This η^2 -ligation appears to stabilize the coordination of $\text{Ph}_2\text{CPz}'_2$ in forming $[\text{Mo}(\text{Ph}_2\text{CPz}'_2)(\text{CO})_2(\text{N}_2\text{C}_6\text{H}_4\text{NO}_2\text{-}p)][\text{BPh}_4]$ (2) and $[\text{Mo}(\text{Ph}_2\text{CPz}'_2)(\text{CO})_2(\text{N}_2\text{Ph})][\text{BF}_4]$ (3) from the reaction of 1 with the appropriate diazonium salt but the stabilization seems not strong enough when $[\text{Mo}(\text{P}(\text{OMe})_3)_3(\text{CO})_3]$ is formed from the reaction of 1 with $\text{P}(\text{OMe})_3$. The solid-state structures of 1 and 3 have been determined by X-ray crystallography: 1- CH_2Cl_2 , monoclinic, $P2_1/n$, $a = 11.814(3)$, $b = 11.7929(12)$, $c = 19.460(6)$ Å, $\beta = 95.605(24)^\circ$, $V = 2698.2(11)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.530$ g/cm³, $R = 0.044$, $R_w = 0.036$ based on 3218 reflections with $I > 2\sigma(I)$; 2 (3)-1/2 hexane-1/2 CH_3OH -1/2 H_2O -1 CH_2Cl_2 , monoclinic, $C2/c$, $a = 41.766(10)$, $b = 20.518(4)$, $c = 16.784(3)$ Å, $\beta = 101.871(18)^\circ$, $V = 14076(5)$ Å³, $Z = 8$, $D_{\text{calc}} = 1.457$ g/cm³, $R = 0.064$, $R_w = 0.059$ based on 5865 reflections with $I > 2\sigma(I)$. Two independent cations were found in the asymmetric unit of the crystals of 3. The average distance between the Mo and the two η^2 -ligated carbon atoms is 2.574 Å in 1 and 2.581 and 2.608 Å in 3. The unfavourable disposition of the η^2 -phenyl group with respect to the metal centre in 3 and the rigidity of the η^2 -arene ligation excludes the possibility of any appreciable agostic C–H \rightarrow Mo interaction.

1. Introduction

In 1975, Cotton and his co-workers determined the crystal structure of $[\text{Mo}(\text{Ph}_2\text{BPz}_2)(\text{CO})_2(\eta^3\text{-CH}_2\text{-C}(\text{Me})\text{CH}_2)]$ ($\text{Pz} = \text{pyrazol-1-yl}$) [1] and found that this compound is not merely a formal 16-electron species like $[\text{Mo}(\text{H}_2\text{BPz}'_2)(\text{CO})_2(\eta^3\text{-C}_7\text{H}_7)]$ ($\text{Pz}' = 3,5\text{-dimethylpyrazol-1-yl}$) [2], $[\text{Mo}(\text{Et}_2\text{BPz}_2)(\text{CO})_2(\eta^3\text{-CH}_2\text{C}(\text{Ph})\text{CH}_2)]$ [3], or $[\text{Mo}(\text{Et}_2\text{BPz}_2)(\text{CO})_2(\eta^3\text{-C}_7\text{H}_7)]$ [4] but is in fact genuine. This is because unfavourable steric repulsion between the *ortho*-hydrogen atoms on the phenyl rings and the hydrogen atoms at the third position on two pyrazolyl rings in the presumed 18-electron structure allows C–H \cdots Mo (three-centre-two-electron) interactions. Since we have recently discovered the intramolecular η^2 -arene struc-

ture of $[\text{Mo}(\text{PhHCPz}'_2)(\text{CO})_3]$ (a formal 16-electron compound [5]) and then realized the importance of the substituent effects of diazolylmethane on spectra and structures of the related molybdenum carbonyl derivatives [6], we were prompted by these reports to continue to prepare $\text{Ph}_2\text{CPz}'_2$ and to study the coordination effect of this neutral nitrogen-bidentate ligand, especially in the η^2 -arene complexes, compared with that of PhHCPz'_2 .

2. Experimental section

All manipulations were carried out under prepurified dinitrogen by conventional Schlenk techniques. Solvents were purified by distillation from an appropriate drying agent (ethers, paraffins and arenes from potassium with benzophenone as indicator; halocarbons and acetonitrile from CaH_2 and alcohols from

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the corresponding alkoxide). Diazonium salts, p -NO₂-C₆H₄N₂⁺Cl⁻ and PhN₂⁺BF₄⁻, were prepared following the published procedure [7] and recrystallized from CH₂Cl₂/MeOH before use.

The melting point of Ph₂CPz'₂ was determined on a Mel-Temp apparatus (Laboratory Devices) and is uncorrected. ¹H and ¹³C{¹H} NMR spectra were recorded on Bruker WP-100, AM-200 or AMX-400 NMR spectrometers and calibrated against internal MeSi₄ (TMS) or the deuterated solvent (s, singlet; d, doublet; m, multiplet; br, broad). Infrared spectra were recorded with a Hitachi 270-30 instrument (vs, very strong; s, strong; m, medium; w, weak; br, broad; sh, shoulder). Elemental analysis was by the Microanalytical Service of the Department of Chemistry, National Cheng Kung University.

2.1. Synthesis of Ph₂CPz'₂

A mixture of HPz' (48.4 g, 0.5 mol) and Ph₂CCl₂ (24 g, 0.1 mol) was stirred and heated at 88°C in 200 ml of toluene and 140 ml of triethylamine for three days. The solvents were then removed under vacuum. The resulted solid residue was washed four times with 30 ml of MeOH to remove Et₃NH⁺Cl⁻ and unreacted HPz'. Recrystallization from *n*-heptane gave 26.3 g of white Ph₂CPz'₂ (74%) with a melting point of 211–212°C. Anal. Calcd. for C₂₃H₂₄N₄: C, 77.49; H, 6.80; N, 15.72; found: C, 77.48; H, 6.86; N, 15.71%. ¹H NMR (25°C, CDCl₃, 200 MHz): phenyl protons, δ 7.23 (m, 6H), 6.99 (m, 4H); protons at the ring-4 position, 6.00 (s, 2H); protons of the methyl groups at the ring-3 and -5 positions, 2.21 (s, 6H), 1.56 (s, 6H). ¹³C{¹H} NMR (25°C, CDCl₃, 50 MHz): carbon nuclei at the ring-3 and -5 positions, δ 145.9 (2 C), 142.3 (2 C); *ipso*-carbon nuclei of two phenyl groups, 141.6 (2 C); carbon nuclei of two phenyl groups, 129.8 (4 C), 127.8 (2 C), 127.0 (4 C); carbon nuclei at the ring-4 position, 108.6 (2 C); Ph₂C, 87.7 (1 C); carbon nuclei of the methyl groups at the ring-3 and -5 positions, 13.9 (2 C), 11.8 (2 C).

2.2. Preparation of [Mo(Ph₂CPz'₂)(CO)₃] (1)

A mixture of Ph₂CPz'₂ (1.81 g, 5.1 mmol) and [Mo(CO)₆] (1.32 g, 5.0 mmol) in 50 ml of 1,2-dimethoxyethane (DME) was refluxed at 85°C for 9 h. The solvent was then removed under vacuum. Recrystallization of the solid residue from CH₂Cl₂/hexane gave 1.97 g (74%) of the orange-red solid of 1. Anal. Calcd. for C₂₆H₂₄MoN₄O₃: C, 58.21; H, 4.51; N, 10.44; found: C, 58.07; H, 4.52; N, 10.38%. ¹H NMR (25°C, CDCl₃, 200 MHz): phenyl protons, δ 7.42 (m, 3H), 7.26 (m, 4H), 6.97 (m, 3H); protons at the ring-4 position, 5.99 (s, 2H); methyl protons at the ring-3 and -5 positions, 2.52 (s, 6H), 2.20 (s, 6H). ¹H NMR (25°C,

CD₂Cl₂, 200 MHz): phenyl protons, δ 7.43 (m, 3H), 7.34 (m, 4H), 7.13 (m, 3H); protons at the ring-4 position, 6.03 (s, 2H); methyl protons at the ring-3 and -5 positions, 2.45 (s, 6H), 2.19 (s, 6H). ¹³C{¹H} NMR (253, 298, or 305 K, CD₂Cl₂, 100 MHz): carbonyl carbon nuclei, δ 229.7 (1 C), 224.9 (1 C), 204.1 (1 C); phenyl carbon nuclei, 136.3 (1 C), 132.5 (1 C), 130.0 (1 C), 129.2 (1 C), 128.9 (1 C), 128.6 (1 C), 128.0 (1 C), 126.8 (2 C), 124.4 (1 C), 119.6 (2 C); carbon nuclei at the ring-3 and -5 positions, 154.3 (2 C), 142.5 (2 C); carbon nuclei at the ring-4 position, 110.6 (2 C); methyl carbon nuclei, 16.1 (2 C), 15.6 (2 C). IR (CH₂Cl₂, cm⁻¹): ν (CO) 1918s, 1800vs. IR (KBr, cm⁻¹): ν (CO) 1912s, 1802s, 1782s.

2.3. Reaction between 1 and P(OMe)₃

To a stirred solution of 1 (0.3 mmol) dissolved in CH₂Cl₂ was added P(OMe)₃ (0.5 ml, 4.2 mmol). The solution gradually changed from orange-red to pale yellow. Six hours were needed for conversion to be completed as judged by the disappearance of the 1800 cm⁻¹ band of 1 in the solvent. The solvent and excess P(OMe)₃ were removed under vacuum and the white product was extracted with hexane from the solid residue. Hexane was then removed under reduced pressure to give 0.14 g of [Mo{P(OMe)₃}(CO)₃] (85%), which was later confirmed by comparing the spectral data with those of an authentic sample directly prepared from [Mo(CO)₃(MeCN)₃] and P(OMe)₃ [8]. From the remaining solid residue, recrystallization from CH₂Cl₂/hexane gave 0.08 g (75%) of Ph₂CPz'₂.

2.4. [Mo(Ph₂CPz'₂)(CO)₂(N₂C₆H₄-NO₂-*p*)] [BPh₄] (2)

To a solution of 1 (0.536 g, 1.0 mmol) dissolved in 20 ml of CH₂Cl₂ was added 0.191 g (1.0 mmol) of *p*-NO₂-C₆H₄N₂⁺Cl⁻. The mixture was stirred for 30 min and 0.523 g (1.5 mmol) of NaBPh₄ and 20 ml of MeOH were added. The mixture was stirred for a further 2 h and the solvent was removed, forming a red brown solid. Recrystallization from CH₂Cl₂/hexane gave 0.37 g (76%) of 2 as a deep red solid. Anal. Calcd. for 2-H₂O or C₅₅H₅₀BMoN₇O₅: C, 66.33; H, 5.07; N, 9.85; found: C, 66.37; H, 4.98; N, 9.98%. ¹H NMR (25°C, CDCl₃, 200 MHz): phenyl protons, δ 7.42–6.97 (m, 34H); protons at the ring-4 position, 6.08 (s, 1H), 5.87 (s, 1H); methyl protons at the ring-3 and -5 positions, 2.49 (s, 3H), 2.37 (s, 3H), 2.15 (s, 3H), 2.00 (s, 3H). IR (CH₂Cl₂, cm⁻¹): ν (CO) 2020br, s, 1938br, s. IR (KBr, cm⁻¹): ν (CO) 2012br, s, 1922br, s; ν (NN) (assignment tentative in the absence of ¹⁵N labelling data) 1554s, 1506sh, 1478w cm⁻¹.

2.5. Mo(Ph₂CPz'₂)(CO)₂(N₂Ph)] [BF₄] (3)

To a solution of 1 (0.536 g, 1.0 mmol) dissolved in 20

ml of CH_2Cl_2 was added 0.191 g (1.0 mmol) of $\text{PhN}_2^+\text{BF}_4^-$. The mixture was stirred for 30 min and filtered. The filtrate was treated with 25 ml of Et_2O . The deep red precipitate was collected and washed twice with 10 ml of Et_2O , and dried under vacuum. Yield of **3**: 0.47 g, 67%. Anal. Calcd. for $3 \cdot \text{H}_2\text{O}$ or $\text{C}_{31}\text{H}_{31}\text{BF}_4\text{MoN}_6\text{O}_3$: C, 51.83; H, 4.35; N, 11.70; found: C, 51.98; H, 4.34; N, 11.56%. ^1H NMR (25°C, CDCl_3 , 200 MHz): phenyl protons, δ 7.58–6.93 (m, 15 H); protons at the ring-4 position, 6.35 (s, 1H), 6.26 (s, 1H); methyl protons at the ring-3 and -5 positions, 2.51 (s, 3H), 2.44 (s, 3H), 2.42 (s, 3H), 2.28 (s, 3H). IR (CH_2Cl_2 , cm^{-1}): $\nu(\text{CO})$ 2012br, s, 1924br, s. IR (KBr, cm^{-1}): $\nu(\text{CO})$ 1992br, s, 1902br, s; $\nu(\text{NN})$ (assignment tentative in the absence of ^{15}N labelling data) 1552m, 1478w cm^{-1} .

2.6. X-Ray diffraction study of **1** and **3**

Single crystals were grown from CH_2Cl_2 /hexane at room temperature. For **1**, the single crystals were then found to contain molecules of the solvent CH_2Cl_2 . For **2** and **3**, much difficulty was at first experienced in growing crystals. Two or three apparently good single crystals were eventually obtained in one trial by dissolving **3** in CH_2Cl_2 and then adding a layer of hexane. It was later revealed from the electron-density difference maps that there are some clathrate molecules [9], two independent cations (**3-I**⁺ and **3-II**⁺) and two BF_4^- anions in the crystal used, including one half hexane molecule (hexane contains the inversion centre), one CH_2Cl_2 , one half methanol (the carbon atom occupies the two-fold axis and the oxygen atom the general position, making itself disordered and having an occupancy of 0.5), and one half water (the oxygen atom also occupies the two-fold axis) in the asymmetric unit of **3**. The water oxygen atom was found to be hydrogen

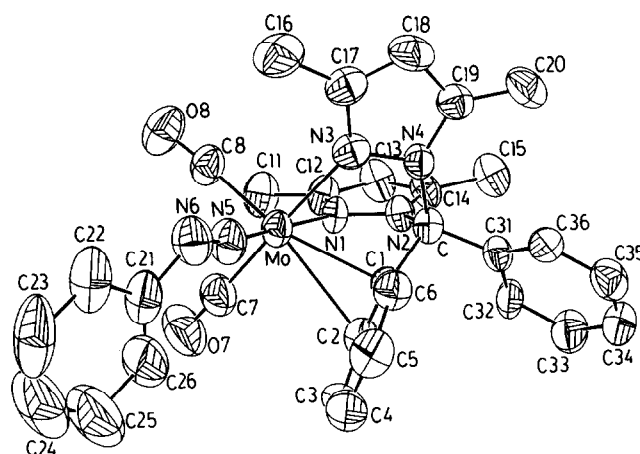


Fig. 2. ORTEP drawing of the cation, $[\text{Mo}(\text{Ph}_2\text{CPz}'_2)(\text{CO})_2(\text{N}_2\text{Ph})]^+$ (**3-I**⁺). Thermal ellipsoids are drawn at the 50% probability level.

bonded to the methanol. The hydrogen atoms for the solvents in **3** were not calculated and were not included in the final refinement of this structure.

General procedures and listings of programs were as previously given [10]. Since the cations, **3-I**⁺ and **3-II**⁺ are similar, the ORTEP drawings with the numbering scheme for **1** and **3-I**⁺ are depicted in Figs. 1 and 2 respectively. The crystallographic details (Table 1), final coordinates of all the non-hydrogen atoms (Table 2), and selected bond lengths and angles for **1** and **3-I**⁺ (Table 3) are reported. In **3**, the non-hydrogen atomic labels for the clathrate molecules are as follows: CH_2Cl_2 , C(40), Cl(1), Cl(2); water, O; MeOH, C(50), O(50); and hexane, C(51), C(52), C(53). Remaining bond lengths and angles, anisotropic displacement coefficient atomic coordinates, the H-atom coordinates, and structure factors for the compounds are available from the authors.

3. Results and discussion

Although neutral nitrogen-bidentate ligands such as H_2CPz_2 or PhHCPz'_2 , derived respectively from pyrazole (HPz) or 3,5-dimethylpyrazole (HPz'), are usually prepared under phase transfer catalysis [11], the typical yields of 42% [12] and 5% [13] found respectively for PhHCPz'_2 and $\text{Ph}_2\text{CPz}'_2$ reflect the different degrees of steric congestion in these compounds and the difficulty in synthesizing them. We therefore modified the procedure, as shown in eqn. (1), to obtain pure $\text{Ph}_2\text{CPz}'_2$ with a yield as high as 74%. PhHCPz'_2 melts at 73–74°C [12] while $\text{Ph}_2\text{CPz}'_2$ melts at 211–212°C, probably indicating that the latter is closer to a sphere in shape and can be packed more regularly in the solid state.

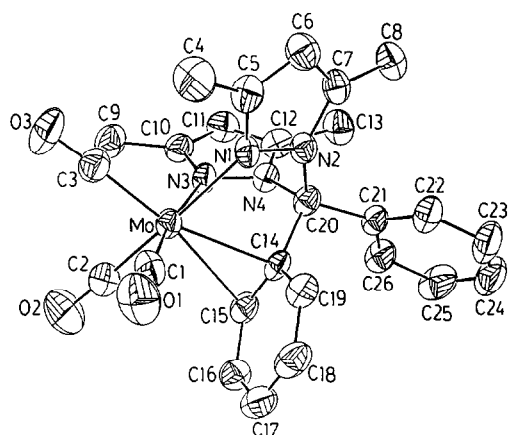
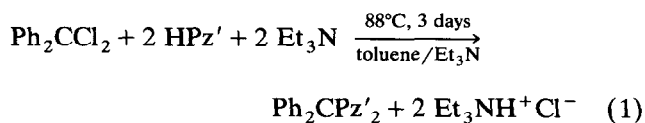
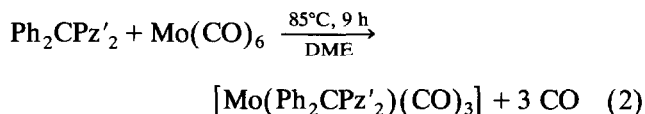


Fig. 1. ORTEP drawing of $[\text{Mo}(\text{Ph}_2\text{CPz}'_2)(\text{CO})_3]$ (**1**). Thermal ellipsoids are drawn at the 50% probability level.



Like $[\text{Mo}(\text{PhHCPz}'_2)(\text{CO})_3]$ [5], $[\text{Mo}(\text{Ph}_2\text{CPz}'_2)(\text{CO})_3]$ (**1**) was obtained from the reaction between $[\text{Mo}(\text{CO})_6]$ and $\text{Ph}_2\text{CPz}'_2$ (eqn. (2)). Both $[\text{Mo}(\text{PhHCPz}'_2)(\text{CO})_3]$ [5] and **1** (Fig. 1) were confirmed by X-ray crystallography to contain η^2 -arene bonding interaction between one π -bond of one phenyl group of the ligand and the metal centre. However, there are the following notable differences in forming the complexes:



(1) the formation of **1** takes 9 h whereas a similar reaction between $[\text{Mo}(\text{CO})_6]$ and PhHCPz'_2 first gave $[\text{Mo}(\text{PhHCPz}'_2)(\text{CO})_4]$ after 1.5 h and then $[\text{Mo}(\text{PhHCPz}'_2)(\text{CO})_3]$ after a subsequent 70 h [5]. Apparently, the repulsive non-bonded interactions between $\text{Ph}_2\text{CPz}'_2$ and *cis*-carbonyls in the presumed intermediate, $[\text{Mo}(\text{Ph}_2\text{CPz}'_2)(\text{CO})_4]$, are larger than those in $[\text{Mo}(\text{PhHCPz}'_2)(\text{CO})_4]$, if such an intermediate is formed during the reaction between $[\text{Mo}(\text{CO})_6]$ and $\text{Ph}_2\text{CPz}'_2$. This argument is compatible with the evidence obtained by comparing the angle formed by the two carbonyls *cis* to the nitrogen bidentate ligand (N–N), which is $166.0(2)^\circ$ in $[\text{Mo}(\text{PhHCPz}'_2)(\text{CO})_4]$ [5] and $167.3(1)^\circ$ in $[\text{Mo}(\text{H}_2\text{CPz}'_2)(\text{CO})_4]$ [14]. Such an angle in the unknown compound $[\text{Mo}(\text{PhHCPz}'_2)(\text{CO})_4]$ should be much larger than $1.3(3)^\circ$, the difference between $166.0(2)^\circ$ and $167.3(1)^\circ$, if the bonding strengths between Mo and N–N are assumed identical. However, as shown below, such an assumption is not justified; upon addition of $\text{P}(\text{OMe})_3$ to **1**, the bonding interactions between N–N and Mo in the presumed intermediate, $[\text{Mo}(\text{Ph}_2\text{CPz}'_2)(\text{CO})_3\text{-P}(\text{OMe})_3]$,

TABLE 1. Crystal data for the η^2 -arene complexes

compound	1	2[3]-solvent ^a
empirical formula	$\text{C}_{27}\text{H}_{26}\text{Cl}_2\text{MoN}_4\text{O}_3$	$\text{C}_{67}\text{H}_{58}\text{B}_2\text{Cl}_2\text{F}_8\text{Mo}_2\text{N}_{12}\text{O}_6$
colour	orange red	deep red
crystal size (mm)	$0.30 \times 0.30 \times 0.35$	$0.45 \times 0.50 \times 0.50$
space group	monoclinic, $P 2_1/n$	monoclinic, $C 2/c$
unit cell dimensions		
<i>a</i> , <i>b</i> , <i>c</i> , Å	11.814(3), 11.7929(12), 19.460(6)	41.766(10), 20.518(4), 16.784(3)
β , deg	95.605(24)	101.871(18)
volume, Å ³	2698.2(11)	14076(5)
<i>Z</i>	4	8
Formula weight	621.37	1543.63
D_{calc} , g/cm ³	1.530	1.457
no. of orientatn rflns	24	24
2θ range, deg	18.80–23.76	18.92–28.12
<i>h</i> , <i>k</i> , <i>l</i> ranges	–14 to 13, 0 to 14, 0 to 23	–44 to 43, 0 to 22, 0 to 18
abs cor		ψ scan
abs coeff, mm ^{–1}	0.71	0.50
transm range	0.9254–0.9981	0.8848–0.9977
$F(000)$	1263.64	6254
diffractometer used		Nonius CAD4
radiation; λ , Å		Mo K α ; 0.70930
temperature (K)		297
scan type		$\theta/2\theta$
2θ range, deg	2–50	2–45
scan speed, deg/min		16.48/2–16.48/7
std rflns		3 std/7200 sec
decay; %	< 2	< 4
no. of unique rflns	4722	9158
no. of rflns (N_o) used	3218 with $I > 2.0\sigma(I)$	5865 with $I > 2.0\sigma(I)$
no. of atoms	63	157
no. of params (N_v) refined	334	885
max Δ/σ ratio	0.094	0.072
<i>R</i> , <i>R</i> _w , <i>S</i> ^b	0.044, 0.036, 2.01	0.064, 0.059, 3.57
resid peak; hole, e/Å ³	0.78, –0.58	0.94, –1.07

^a solvent = 1/2 hexane 1/2CH₃OH-1/2H₂O-1CH₂Cl₂, see text. ^b $S = [\sum \omega |F_o - F_c|^2 / (N_o - N_v)]^{1/2}$

TABLE 2. Final coordinates of the non-hydrogen atoms for 1 and 3^a

Atom	x	y	z	$B_{\text{iso}}, \text{\AA}^2$ ^b	Atom	x	y	z	$B_{\text{iso}}, \text{\AA}^2$
<i>(a) Compound 1</i>									
Mo	0.29848(4)	0.03149(4)	0.13349(3)	2.738(20)	N(1)	0.1705(4)	0.1660(4)	0.15991(21)	2.86(20)
N(2)	0.1515(4)	0.2545(4)	0.11398(21)	2.73(20)	N(3)	0.2075(4)	0.0678(3)	0.02774(21)	2.79(21)
N(4)	0.1949(4)	0.1795(4)	0.00743(21)	2.68(20)	C(1)	0.3786(5)	0.0257(5)	0.2246(3)	3.6(3)
O(1)	0.4284(4)	0.0239(4)	0.27958(20)	5.9(3)	C(2)	0.4011(5)	-0.0812(5)	0.1055(3)	3.6(3)
O(2)	0.4630(4)	-0.1526(4)	0.08997(23)	6.1(3)	C(3)	0.2126(5)	-0.0960(5)	0.1592(3)	3.7(3)
O(3)	0.1640(4)	-0.1773(4)	0.17476(23)	5.8(3)	C(4)	0.0770(6)	0.0861(6)	0.2570(3)	5.4(4)
C(5)	0.0832(5)	0.1657(5)	0.1971(3)	3.5(3)	C(6)	0.0058(5)	0.2492(5)	0.1738(3)	3.8(3)
C(7)	0.0480(5)	0.3033(5)	0.1202(3)	3.1(3)	C(8)	-0.0092(5)	0.3924(5)	0.0759(3)	4.0(3)
C(9)	0.1500(5)	-0.1197(5)	-0.0192(3)	4.1(3)	C(10)	0.1520(4)	0.0068(5)	-0.0229(3)	3.2(3)
C(11)	0.1008(5)	0.0782(5)	-0.0723(3)	3.6(3)	C(12)	0.1256(5)	0.1870(5)	-0.0534(3)	3.2(3)
C(13)	0.0833(5)	0.2936(5)	-0.0891(3)	3.9(3)	C(14)	0.3510(4)	0.2226(4)	0.0967(3)	2.70(24)
C(15)	0.4284(5)	0.1636(5)	0.0608(3)	3.08(25)	C(16)	0.5437(5)	0.1585(5)	0.0866(3)	3.9(3)
C(17)	0.5809(5)	0.2125(6)	0.1468(3)	4.3(3)	C(18)	0.5048(5)	0.2691(5)	0.1839(3)	4.2(3)
C(19)	0.3917(5)	0.2741(5)	0.1603(3)	3.4(3)	C(20)	0.2340(4)	0.2608(4)	0.0618(3)	2.73(23)
C(21)	0.2563(5)	0.3807(5)	0.0360(3)	3.01(24)	C(22)	0.2420(5)	0.4739(5)	0.0771(3)	3.9(3)
C(23)	0.2798(6)	0.5790(5)	0.0589(3)	5.0(3)	C(24)	0.3350(6)	0.5913(5)	0.0007(4)	5.8(4)
C(25)	0.3528(5)	0.4994(6)	-0.0399(3)	5.1(3)	C(26)	0.3147(5)	0.3923(5)	-0.0216(3)	4.0(3)
C(27)	0.6727(7)	0.9306(7)	0.2006(4)	8.5(5)	Cl(1)	0.70342(19)	0.78673(20)	0.19812(11)	7.84(13)
Cl(2)	0.7498(3)	0.9947(3)	0.26728(20)	16.7(3)					
<i>(b) Compound 3</i>									
<i>(i) Cation 3-I⁺</i>									
Mo	0.11904(3)	0.09932(5)	0.13014(6)	3.69(5)	N(1)	0.13225(20)	0.1990(4)	0.0997(5)	3.6(5)
N(2)	0.15656(20)	0.2050(4)	0.0573(5)	3.3(5)	N(3)	0.17352(21)	0.0908(4)	0.1592(5)	4.0(5)
N(4)	0.19098(20)	0.1166(4)	0.1052(5)	3.5(4)	C	0.16979(25)	0.1433(5)	0.0326(6)	3.1(5)
C(1)	0.14164(25)	0.0933(5)	0.0055(6)	3.3(6)	C(2)	0.1112(3)	0.1130(5)	-0.0355(7)	4.2(6)
C(3)	0.0889(3)	0.0663(6)	-0.0788(7)	5.0(7)	C(4)	0.0978(3)	0.0033(6)	-0.0822(7)	5.4(7)
C(5)	0.1282(3)	-0.0151(6)	-0.0392(7)	5.3(8)	C(6)	0.1500(3)	0.0278(5)	0.0035(7)	4.2(6)
C(7)	0.0713(3)	0.1191(6)	0.0997(7)	5.6(7)	O(7)	0.04378(21)	0.1298(5)	0.0848(6)	8.3(6)
C(8)	0.1132(3)	0.1177(5)	0.2380(7)	4.6(7)	O(8)	0.10774(23)	0.1285(4)	0.3025(5)	6.9(6)
C(11)	0.1006(3)	0.2743(6)	0.1687(7)	5.5(7)	C(12)	0.1270(3)	0.2596(5)	0.1246(7)	4.2(6)
C(13)	0.1485(3)	0.3031(5)	0.1005(7)	4.8(7)	C(14)	0.1673(3)	0.2673(5)	0.0596(7)	4.0(6)
C(15)	0.1954(3)	0.2923(6)	0.0292(7)	5.1(7)	C(16)	0.1848(3)	0.0442(7)	0.2979(8)	6.8(8)
C(17)	0.1951(3)	0.0755(5)	0.2266(7)	4.5(6)	C(18)	0.2261(3)	0.0929(6)	0.2165(7)	5.0(7)
C(19)	0.2229(3)	0.1206(5)	0.1413(6)	3.9(6)	C(20)	0.2499(3)	0.1492(6)	0.1093(7)	5.5(7)
N(5)	0.10989(23)	0.0141(4)	0.1522(6)	4.7(5)	N(6)	0.10639(24)	-0.0400(5)	0.1766(6)	5.5(6)
C(21)	0.0768(3)	-0.0749(6)	0.1546(7)	5.8(8)	C(22)	0.0743(4)	-0.1288(6)	0.2043(8)	7.2(9)
C(23)	0.0441(4)	-0.1626(7)	0.1876(10)	10.0(12)	C(24)	0.0200(4)	-0.1425(8)	0.1223(11)	12.4(13)
C(25)	0.0235(4)	-0.0886(8)	0.0746(11)	11.6(13)	C(26)	0.0529(4)	-0.0562(7)	0.0930(9)	8.0(9)
C(31)	0.18440(25)	0.1520(5)	-0.0411(6)	3.4(6)	C(32)	0.1687(3)	0.1938(6)	-0.1018(7)	4.4(6)
C(33)	0.1790(3)	0.1981(6)	-0.1741(7)	5.6(8)	C(34)	0.2036(3)	0.1601(6)	-0.1894(7)	5.8(8)
C(35)	0.2186(3)	0.1167(6)	-0.1298(7)	4.9(7)	C(36)	0.2083(3)	0.1112(6)	-0.0560(6)	4.1(6)
<i>(ii) Cation 3-II⁺</i>									
Mo	0.40401(3)	0.21096(5)	0.54417(6)	3.96(5)	N(1)	0.43802(21)	0.1849(4)	0.4666(5)	3.8(5)
N(2)	0.42631(21)	0.1509(4)	0.3950(5)	3.6(5)	N(3)	0.39460(20)	0.1042(4)	0.5284(5)	3.5(5)
N(4)	0.39204(20)	0.0794(4)	0.4509(5)	3.4(4)	C	0.39141(25)	0.1301(5)	0.3879(6)	3.4(6)
C(1)	0.3713(3)	0.1893(5)	0.4079(6)	3.2(5)	C(2)	0.3794(3)	0.2531(5)	0.3907(7)	4.1(6)
C(3)	0.3563(3)	0.3034(6)	0.3901(7)	5.5(8)	C(4)	0.3267(3)	0.2889(7)	0.4051(8)	6.1(8)
C(5)	0.3181(3)	0.2277(6)	0.4213(7)	5.3(7)	C(6)	0.3399(3)	0.1777(5)	0.4224(7)	4.2(6)
C(7)	0.4202(3)	0.3054(6)	0.5496(7)	5.6(8)	O(7)	0.4307(3)	0.3562(4)	0.5574(6)	9.4(7)
C(8)	0.4333(3)	0.2017(6)	0.6496(7)	5.4(7)	O(8)	0.45178(21)	0.2002(5)	0.7126(5)	7.7(6)
C(11)	0.4927(3)	0.2262(7)	0.5380(8)	7.1(9)	C(12)	0.4707(3)	0.1908(6)	0.4708(7)	4.9(7)
C(13)	0.4801(3)	0.1594(6)	0.4055(7)	5.4(7)	C(14)	0.4518(3)	0.1328(5)	0.3579(7)	4.3(7)
C(15)	0.4506(3)	0.0928(6)	0.2836(7)	5.5(7)	C(16)	0.4022(3)	0.0565(6)	0.6650(7)	5.9(8)
C(17)	0.3997(3)	0.0517(5)	0.5774(6)	4.1(6)	C(18)	0.4018(3)	-0.0041(5)	0.5327(7)	4.3(6)
C(19)	0.3980(3)	0.0145(5)	0.4545(7)	3.8(6)	C(20)	0.3997(3)	-0.0288(6)	0.3848(7)	5.4(8)
N(5)	0.36946(23)	0.2391(4)	0.5894(5)	4.7(5)	N(6)	0.34601(23)	0.2645(5)	0.6092(6)	5.4(6)

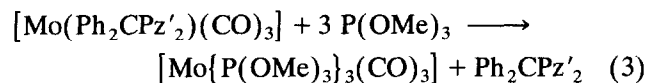
TABLE 2 (Continued)

Atom	x	y	z	$B_{\text{iso}}, \text{\AA}^2$ ^b	Atom	x	y	z	$B_{\text{iso}}, \text{\AA}^2$
(ii) Cation 3-II ⁺									
C(21)	0.3264(3)	0.2267(6)	0.6512(7)	4.8(7)	C(22)	0.3271(4)	0.1621(7)	0.6548(11)	9.3(12)
C(23)	0.3086(4)	0.1276(8)	0.6986(12)	12.9(15)	C(24)	0.2870(4)	0.1612(8)	0.7325(11)	10.7(13)
C(25)	0.2841(3)	0.2271(8)	0.7257(9)	8.3(10)	C(26)	0.3050(3)	0.2593(6)	0.6860(8)	6.7(8)
C(31)	0.37441(25)	0.1098(5)	0.3019(6)	3.5(6)	C(32)	0.3801(3)	0.1422(5)	0.2328(7)	4.2(6)
C(33)	0.3615(3)	0.1282(6)	0.1560(6)	4.7(6)	C(34)	0.3370(3)	0.0836(6)	0.1483(7)	4.9(7)
C(35)	0.3295(3)	0.0548(6)	0.2149(7)	5.2(7)	C(36)	0.3477(3)	0.0674(5)	0.2922(7)	4.4(7)
(iii) Anions BF_4^- and the clathrate molecules									
B(1)	0.7045(4)	-0.0069(8)	0.0731(11)	6.9(11)	F(1)	0.72085(19)	-0.0395(4)	0.0211(5)	8.5(5)
F(2)	0.68299(22)	0.0342(4)	0.0234(6)	11.2(7)	F(3)	0.6836(3)	-0.0470(5)	0.0991(7)	15.9(10)
F(4)	0.72169(24)	0.0246(6)	0.1277(7)	17.1(9)	B(2)	0.4313(4)	0.2208(9)	0.0844(11)	8.4(12)
F(5)	0.44389(21)	0.2652(4)	0.0432(6)	11.3(7)	F(6)	0.4553(3)	0.2173(6)	0.1561(6)	15.1(9)
F(7)	0.40423(20)	0.2393(4)	0.1016(7)	13.1(8)	F(8)	0.4323(3)	0.1621(5)	0.0585(8)	15.7(10)
C(40)	0.7551(6)	0.4138(11)	1.0337(16)	21.5(23)	Cl(1)	0.73426(20)	0.3465(4)	0.9901(5)	23.4(8)
Cl(2)	0.73187(15)	0.4472(3)	1.1010(4)	15.6(5)	O	0	0.1262(12)	0.25	19.0(20)
C(50)	0	0.0166(11)	0.25	12.7(20)	O(50) ^c	-0.0160(5)	0.0446(12)	0.2023(15)	15.5(19)
C(51)	0.9999(6)	0.4410(11)	0.1563(17)	25.1(27)	C(52)	0.9935(4)	0.4695(9)	0.0881(13)	17.3(16)
C(53)	0.9846(3)	0.5003(10)	0.0076(14)	12.1(12)					

^a The crystal of **3** contains two cations, 3-I⁺ and 3-II⁺, two anions, BF_4^- , and the clathrate molecules; see Text. ^b B_{iso} is the mean of the principal axes of the thermal ellipsoid. ^c Occupancy = 0.50.

become weak, eventually (*ca.* 6 h later) leading to the displacement of N-N by two other $\text{P}(\text{OMe})_3$ molecules at room temperature (eqn. (3));

(2) the average distance, d , between Mo and the two η^2 -ligated carbon atoms is 2.574 Å in **1**, much shorter than that of 2.803 Å in $[\text{Mo}(\text{PhHCPz}'_2)(\text{CO})_3]$ [5], although both are relatively long compared with the typical value of 2.4 Å for a $\text{Mo}^0\text{-C}(\text{sp}^2)$ bond [15]. The expected sum of the van der Waals radii is *ca.* 3.6 Å for $\text{Mo}^0 \cdots \text{C}(\text{sp}^2)$ [16]. Based on the average value of 1.373 Å from the six C-C distances found in the structure of $[\text{Mo}(\text{PhHCPz}'_2)(\text{CO})_4]$ [5] and on the η^2 -bonded C=C distances of 1.402(6) Å in $[\text{Mo}(\text{PhHCPz}'_2)(\text{CO})_3]$ [5] and 1.391(8) Å in **1**, the η^2 -complexed C=C bond is lengthened by 0.029(6) Å in $[\text{Mo}(\text{PhHCPz}'_2)(\text{CO})_3]$, much longer than that of 0.018(8) Å in **1**.



Why is there a relatively small elongation at a much shorter d in **1** compared with what is seen in $[\text{Mo}(\text{PhHCPz}'_2)(\text{CO})_3]$? Although one may argue that this is one result of the complicated electronic factors involved in the two complexes, we cannot exclude the possibility that the short d in **1** is a forced result; as there is more steric repulsion between two phenyl groups in **1** than between one H atom and one phenyl group in $[\text{Mo}(\text{PhHCPz}'_2)(\text{CO})_3]$ this forces one phenyl group in **1** to approach closer to Mo than does the phenyl group in $[\text{Mo}(\text{PhHCPz}'_2)(\text{CO})_3]$. By comparing

the distances, d , of 2.608 and 2.581 Å, found in $[\text{Mo}(\text{Ph}_2\text{CPz}'_2)(\text{CO})_2(\text{N}_2\text{Ph})][\text{BF}_4^-]$, stated below, the "forced" d should be around 2.6 Å.

This argument can also be supported as follows. Since **1** and $[\text{Mo}(\text{PhHCPz}'_2)(\text{CO})_3]$ are the intramolecular η^2 -arene complexes using *ipso*- and *ortho*-carbon atoms, the distance, d' , between Mo and the *ipso*-carbon atom (C_i) should be shorter than the other one, d'' , between Mo and the *ortho*-carbon atom (C_o): (d' , d'') 2.766(4), 2.840(4) Å in $[\text{Mo}(\text{PhHCPz}'_2)(\text{CO})_3]$ and 2.462(5), 2.685(5) Å in **1**. As expected, the two carbon atoms are found not to be coplanar with the other four carbon atoms in the η^2 -ligated phenyl group in the two compounds. If a least-square plane is calculated for these atoms, it is found that the perpendicular distances from C_i and C_o atoms respectively to this plane are 0.017 and 0.028 Å in $[\text{Mo}(\text{PhHCPz}'_2)(\text{CO})_3]$ but 0.044 and 0.024 Å in **1**. Apparently, steric repulsion distorts the disposition of the C_i atom in **1** more than that in $[\text{Mo}(\text{PhHCPz}'_2)(\text{CO})_3]$. It is also worth noting that the perpendicular distance between Mo and the plane is found as -2.346 Å in **1** and -2.555 Å in $[\text{Mo}(\text{PhHCPz}'_2)(\text{CO})_3]$ [5] with the negative values indicating in both compounds that the η^2 -ligated C=C bond folds slightly out of the metal centre. Obviously, this specific feature is also another steric effect and is related to the fact that the two complexes do not involve inter- but intramolecular η^2 -arene ligation;

(3) by considering the size difference between CO (with a cone angle of 95° [17]) and $\text{P}(\text{OMe})_3$ (with a cone angle of 107° [17]), the different steric repulsion

TABLE 3. Selected bond lengths (Å) and angles (°) for structures 1 and 3-I⁺

(a) Structure 1			
<i>(i) Bond lengths</i>			
Mo–N(1)	2.284(4)	Mo–N(3)	2.267(4)
Mo–C(1)	1.928(5)	Mo–C(2)	1.913(6)
Mo–C(3)	1.908(6)	C(14)–C(15)	1.391(8)
Mo–C(14)	2.462(5)	C(14)–C(19)	1.420(7)
Mo–C(15)	2.685(5)	C(14)–C(20)	1.547(7)
N(1)–N(2)	1.378(6)	C(15)–C(16)	1.407(8)
C(16)–C(17)	1.368(9)	C(17)–C(18)	1.378(9)
C(18)–C(19)	1.371(8)	N(2)–C(20)	1.476(7)
C(20)–C(21)	1.532(7)	N(3)–N(4)	1.379(6)
N(4)–C(20)	1.469(7)	C(1)–O(1)	1.170(7)
C(2)–O(2)	1.174(7)	C(3)–O(3)	1.172(7)
<i>(ii) Bond angles</i>			
N(1)–Mo–N(3)	78.92(15)	N(1)–Mo–C(1)	95.41(20)
N(1)–Mo–C(2)	176.37(20)	N(1)–Mo–C(3)	96.17(21)
N(1)–Mo–C(14)	67.74(17)	N(1)–Mo–C(15)	98.09(16)
N(3)–Mo–C(1)	171.14(21)	N(3)–Mo–C(2)	97.47(20)
N(3)–Mo–C(3)	99.80(20)	N(3)–Mo–C(14)	70.97(16)
N(3)–Mo–C(15)	69.92(15)	C(1)–Mo–C(2)	88.23(24)
Mo–C(14)–C(15)	83.4(3)	C(1)–Mo–C(3)	87.50(25)
Mo–C(14)–C(19)	102.2(3)	C(1)–Mo–C(14)	100.65(22)
Mo–C(14)–C(20)	98.9(3)	C(1)–Mo–C(15)	104.51(21)
C(15)–C(14)–C(19)	118.0(5)	C(2)–Mo–C(3)	84.00(25)
C(15)–C(14)–C(20)	121.9(4)	C(2)–Mo–C(14)	111.60(21)
C(19)–C(14)–C(20)	118.0(5)	C(2)–Mo–C(15)	80.92(21)
Mo–C(15)–C(14)	65.6(3)	C(3)–Mo–C(14)	162.40(22)
Mo–C(15)–C(16)	111.7(4)	C(3)–Mo–C(15)	160.33(21)
C(14)–C(15)–C(16)	120.2(5)	C(14)–Mo–C(15)	30.96(17)
C(15)–C(16)–C(17)	120.3(5)	Mo–N(1)–N(2)	116.7(3)
C(16)–C(17)–C(18)	120.2(5)	C(17)–C(18)–C(19)	120.6(5)
C(14)–C(19)–C(18)	120.6(5)	N(2)–C(20)–N(4)	106.3(4)
N(2)–C(20)–C(14)	107.7(4)	N(1)–N(2)–C(20)	114.1(4)
N(2)–C(20)–C(21)	114.7(4)	N(4)–C(20)–C(14)	109.3(4)
N(4)–C(20)–C(21)	114.8(4)	C(14)–C(20)–C(21)	103.8(4)
Mo–N(3)–N(4)	118.0(3)	N(3)–N(4)–C(20)	113.6(4)
Mo–C(1)–O(1)	178.8(5)	Mo–C(2)–O(2)	177.8(5)
Mo–C(3)–O(3)	177.0(5)		
<i>(b) Structure 3-I⁺</i>			
<i>(i) Bond lengths</i>			
Mo–N(1)	2.205(8)	Mo–N(3)	2.234(9)
Mo–C(7)	1.996(12)	Mo–C(8)	1.913(11)
Mo–C(1)	2.469(10)	Mo–C(2)	2.747(11)
Mo–N(5)	1.844(9)	N(1)–N(2)	1.360(11)
N(2)–C	1.475(13)	N(3)–N(4)	1.381(12)
N(4)–C	1.457(13)	C–C(1)	1.556(14)
C–C(31)	1.498(14)	C(1)–C(2)	1.374(15)
C(1)–C(6)	1.391(15)	C(2)–C(3)	1.426(16)
C(3)–C(4)	1.349(17)	C(4)–C(5)	1.380(18)
C(5)–C(6)	1.360(16)	C(7)–O(7)	1.145(15)
C(8)–O(8)	1.173(13)	N(5)–N(6)	1.202(13)
N(6)–C(21)	1.411(16)		
<i>(ii) Bond angles</i>			
N(1)–Mo–N(3)	80.3(3)	N(1)–Mo–C(7)	92.1(4)
N(1)–Mo–C(8)	97.0(4)	N(1)–Mo–N(5)	176.4(4)
N(3)–Mo–C(7)	172.3(4)	N(3)–Mo–C(8)	97.5(4)
N(3)–Mo–N(5)	97.2(4)	C(7)–Mo–C(8)	83.6(5)

TABLE 3 (Continued)

<i>(b) Structure 3-I⁺</i>			
<i>(ii) Bond angles</i>			
C(7)–Mo–N(5)	90.4(5)	C(8)–Mo–N(5)	85.7(4)
Mo–N(1)–N(2)	117.0(6)	N(1)–N(2)–C	115.6(8)
Mo–N(3)–N(4)	118.6(6)	N(3)–N(4)–C	112.4(8)
N(2)–C–N(4)	106.6(8)	N(2)–C–C(1)	110.1(8)
N(2)–C–C(31)	111.7(8)	N(4)–C–C(1)	106.8(8)
N(4)–C–C(31)	117.0(8)	C(1)–C–C(31)	104.4(8)
<i>(i) Bond lengths</i>			
C–C(1)–C(2)	121.2(9)	C–C(1)–C(6)	117.7(9)
C(2)–C(1)–C(6)	118.9(10)	C(1)–C(2)–C(3)	119.8(10)
C(2)–C(3)–C(4)	120.6(11)	C(3)–C(4)–C(5)	118.0(11)
C(4)–C(5)–C(6)	122.9(11)	C(1)–C(6)–C(5)	119.6(10)
Mo–C(7)–O(7)	177.7(10)	Mo–C(8)–O(8)	176.0(10)
Mo–N(5)–N(6)	171.4(9)	N(5)–N(6)–C(21)	122.8(11)
N(6)–C(21)–C(22)	114.4(12)	N(6)–C(21)–C(26)	122.0(11)
C–C(31)–C(32)	117.9(9)	C–C(31)–C(36)	121.0(9)
Mo–C(1)–C(2)	86.3(6)	Mo–C(1)–C(6)	102.2(7)
Mo–C(2)–C(1)	63.8(6)	Mo–C(2)–C(3)	112.1(7)
<i>(iii) Torsion angle</i>			
		Mo–N(5)–N(6)–C(21)	37.0(10)

between N–N and *cis*-carbonyls in [Mo(N–N)(CO)₃L] (L = CO or P(OMe)₃) and that between the substituents in N–N as well as the weak η^2 -arene ligation in the compounds, it is no surprise to observe that P(OMe)₃ reacted with [Mo(PhHCPz'₂)(CO)₃] to give [Mo(PhHCPz'₂)(CO)₃(P(OMe)₃)] [5] while converting 1 into [Mo{P(OMe)₃}(CO)₃] (eqn. (3)).

The ¹³C{¹H} NMR spectra of 1 measured between 253–305 K each contains ten phenyl-carbon singlets and three carbonyl-carbon signals, indicating that the weakly η^2 -ligated phenyl group does not change with the other phenyl moiety in solution within NMR time scale. If the η^2 -bonding group can be regarded as one coordination site around the central metal atom, this rigidity probably reflects the propensity of the organo-transition metal complexes to have six two-electron donors to fill all the low-lying molecular orbitals of the resulted pseudo-octahedral geometry [18].

Upon addition of arene (Ar) diazonium salts, deep red compounds, [Mo(Ph₂CPz'₂)(CO)₂(N₂-C₆H₄-NO₂-p)][BPh₄] (2) and [Mo(Ph₂CPz'₂)(CO)₂(N₂Ph)][BF₄] (3), were obtained. The solid-state structure of the latter compound has also been determined by X-ray crystallography to have a similar η^2 -ligation. To our surprise, there are two cations, 3-I⁺ and 3-II⁺, with a similar η^2 -geometry (Fig. 2), two BF₄[−] anions, and several other clathrate molecules, including water, CH₂Cl₂, MeOH and hexane, in the asymmetric unit of the crystal used. The major difference between the geometries of 3-I⁺ and 3-II⁺ is the relative orientation of the (N–N)Mo(CO)₂ fragment with respect to the

N_2Ar moiety, as shown in the torsion angle, defined by Mo–N–N–Ar, of 37° in the former structure and 28° in the latter one. Since we failed in many trials to obtain good single crystals for **2** and **3**, though we eventually got two or three apparently good ones for the latter, it appears that different solvent molecules (and water) are needed to fill the vacancies after the packing of the two cations and two anions of **3** together [9] to form the single crystals. Since the MeOH molecules in the crystals of **3** come from the recrystallization solvents used for the diazonium salt before its reaction with **1**, it may therefore be that addition of MeOH on recrystallization of **3**, as pointed out by one referee, will give a greater amount of good crystals. Following the similarity in both IR and NMR spectra of the two compounds, **2** should also be another η^2 -arene compound. The IR bands tentatively assigned to $\nu(NN)$ for **2** or **3** in a KBr disc also seem compatible with the presence of isomers but this assignment is subject to confirmation by ^{15}N labelling studies.

Analogous to **1** (Fig. 1), the coordination of the molybdenum atom in either cation, **3-I**⁺ or **3-II**⁺ (Fig. 2), is also pseudo-octahedral. The N_2Ar group is *trans* to one pyrazolyl ring. The Mo–N–N and N–N–Ar angles are $171.4(9)^\circ$ and $122.8(11)^\circ$, respectively, in **3-I**⁺ and $169.8(8)^\circ$ and $118.8(10)^\circ$, respectively, in **3-II**⁺, indicating that the arenediazo ligand in both cations has a “singly bent” geometry [19]. The N–N distances (1.202(13) and 1.214(13) Å) are also within the range previously established for the singly bent coordination mode [20–23]. The Mo– N_2Ar distances (1.844(9) and 1.856(9) Å) in **3** are longer than the reported values of 1.78(1) Å in $[MoCl(N_2COPh)(NHNCOPh)(PMe_2Ph)_2]$ [20], 1.807(8) Å in $[Mo(HBPz_3)(SC_6H_4Me_p)_2(N_2C_6H_4F_p)]$ [21] but comparable to the values of 1.825(4) Å in $[Mo(HBPz_3)(CO)_2(N_2Ph)]$ [22], and 1.826(2) Å and 1.834(3) Å in $[Mo(\eta^5Me-C_5H_4)Cl(N_2C_6H_4F)_2]$ [23]. Since the Mo–N(arenediazo) distances in **3** are significantly shorter than the typical single-bond distances such as the Mo–N(pyrazolyl) values of 2.205(8), 2.234(9), 2.182(8), 2.231(8) Å found in **3** or those of 2.284(4), 2.267(4) in **1** (Table 3), a substantial contribution of the resonance structure, Mo=N⁺=N–Ar, is present for the singly-bent arenediazo groups in **3**. The arenediazo ligand in **3** (and in **2**) can thus be regarded as either a formal four-electron donor, $[ArN_2]^-$, to Mo^{II} or a formal two-electron donor, $[ArN_2]^+$, to Mo⁰ with strong back-donation from the metal to the ligand N–N π^* orbitals.

It is therefore true that the formal 14-electron compound, **2** or **3**, is in fact the 18-electron species with consideration of the η^2 -arene and the arenediazo bonding interactions. However, the average distances

between Mo and the two η^2 -ligated carbon atoms in **3-I**⁺ and **3-II**⁺, are 2.608 and 2.581 Å, respectively, longer than that of 2.574 Å in **1**. This shows that the η^2 -bonding interaction is weaker for **3**. Consistently, by comparing with the averaged value of 1.373 Å from the six C–C distances found in the structure of $[Mo(PhHCPz'_2)(CO)_4]$ [5], the η^2 -ligated C=C bond lengths of 1.372(16) Å in **3-I**⁺ and 1.392(16) Å in **3-II**⁺, respectively, indicate that there is no elongation in **3-I**⁺ and almost no elongation in **3-II**⁺. Thus, this observation is compatible with one conclusion previously reported for either intra- or intermolecular η^2 -arene complexes that it is the back-donation from the central metal atom to η^2 -arene π^* orbitals that determines the elongation of the η^2 -ligated C=C bond length [24]. The arenediazo ligand in **3** (and in **2**) should hence be regarded as a formal four-electron donor, $[ArN_2]^-$, to Mo^{II} and the negligible elongation in **3** is due to the impossibility of Mo^{II} back-donation to the η^2 -ligated C=C bond.

Is there any possibility that the *ortho*-hydrogen atoms of the η^2 -phenyl group in **1** or **3** interact appreciably with the metal centre to give an agostic C–H \rightarrow Mo interaction [25]? Although the *d* values of 2.574–2.608 Å in **1** or **3** are close to the range previously reported for such interactions, a careful check of the structures reveals that the disposition of the conformation with respect to the metal centre is not favourable for any appreciable agostic C–H \rightarrow Mo interactions. Further, the rigidity of the η^2 -arene ligation, as shown in the variable-temperature ^{13}C NMR data for **1**, inhibits opportunity for any readjustment of the conformation in solution. Though it is possible that heating of **1–3** may overcome the energy barrier of the weak η^2 -arene ligation, the compounds are found to be almost insoluble in non-coordinating solvents with high boiling points and no successful experiments in this respect can be reported. To this end, we are currently investigating other metal-ligand systems and any positive results will be reported.

4. Conclusion

$Ph_2CPz'_2$, which is bulkier than $PhHCPz'_2$, converts $[Mo(CO)_6]$ more readily into the η^2 -arene compounds, $[Mo(N-N)(CO)_3]$ ($N-N = Ph_2CPz'_2$ or $PhHCPz'_2$). This η^2 -ligation appears to stabilize the coordination of $Ph_2CPz'_2$ in forming $[Mo(Ph_2CPz'_2)(CO)_2(N_2C_6H_4NO_{2-p})][BPh_4]$ (**2**) and $[Mo(Ph_2CPz'_2)(CO)_2(N_2Ph)][BF_4]$ (**3**) from the reaction of **1** with the appropriate diazonium salt but the stabilization seems not strong enough to form $[Mo(P(OMe)_3)_3(CO)_3]$ from the reaction of **1** with $P(OMe)_3$. The unfavourable disposition of the η^2 -phenyl group with respect to the metal centre in **3** and the rigidity of the η^2 -arene ligation

excludes the possibility of an appreciable agostic C–H \rightarrow Mo interaction.

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