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Structural and Spectroscopic Studies of $Mo_2Cl_4(PR_3)_4$ Compounds with Phosphines of Varied Basicity

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Abstract

The influence of the π acidity of the PR_3 ligands in $Mo_2Cl_4(PR_3)_4$ compounds on the strength of the Mo–Mo quadruple bond has been studied for twenty such compounds. The main result is that reasonable correlations exist between the $\delta \rightarrow \delta^*$ transition energy (TE) and two accepted measures of π-acidity for phosphine ligands, namely Tolman's $\bar{\nu}$(CO) IR criterion and Bodner's $\Delta\delta$(CO) ^{13}C NMR criterion. For a plot of TE *versus* $\bar{\nu}$(CO) a correlation coefficient of –0.892 was obtained employing data for 15 compounds. For TE *versus* $\Delta\delta$(CO), a correlation coefficient of 0.982 was obtained for 13 compounds (excluding three for which a steric factor may be important). An attempt to correlate the Mo–Mo bond lengths with π-acidity was unsuccessful since few compounds were obtained in satisfactory form for structure determination, and for the four compounds with known structure there was no correlation. In addition to the PMe_3 compound whose structure was previously known, those of the PEt_3, PMe_2Ph and $PHPh_2$ compounds have been determined and are reported here.

Introduction

Quadruple bonds are measurably sensitive to the electronic properties of the ligands attached to the metal atoms. The influence of ligand properties can be detected by measurements of both structural and spectroscopic characteristics of the bonds [1]. One effect that is of particular interest is the influence of ligand π acidity on the strength of the π and δ components of the metal–metal bond. As noted elsewhere [2], this influence is exerted because empty ligand π orbitals can interact with, and remove electron density from, the M–M π and δ orbitals. With extremely powerful π acids, the influence is so strong as to destabilize the bond entirely so that only mononuclear products are obtained when Mo–Mo or Re–Re quadruple bonds are treated with the potential ligands CO, NO, or RNC.

In the present work we have attempted to study the action of π-acidic ligands on M–M quadruple bonds in such a way that the bonds would remain intact but show quantitatively measurable responses to ligands of varying π-acceptor abilities. Our intention was to employ both M–M bond length variations (measured by X-ray crystallographic studies) and $\delta \rightarrow \delta^*$ transition energies (measured spectroscopically) as indicators of the variations in metal–ligand π interactions. The structural approach had only limited success because most of the compounds proved difficult to crystallize. The spectroscopic approach was more productive, allowing us to employ fifteen different PR_3 type ligands, covering a considerable range of π-acidities, in compounds of the type $Mo_2Cl_4(PR_3)_4$. We report here both the structural and spectroscopic results.

Experimental

Starting Materials

$(NH_4)_5[Mo_2Cl_8]Cl \cdot H_2O$, $Mo_2(O_2CCH_3)_4$ and $Mo_2(O_2CCF_3)_4$ were prepared by established procedures [3–5]. Phosphines and chlorotrimethylsilane were obtained from commercial sources. Solvents used for synthetic reactions and spectral measurements were spectroscopic grade and were deoxygenated by purging with nitrogen for 15–30 min prior to use.

Preparation of Compounds

All reactions were carried out under a nitrogen atmosphere, and reflux reactions were conducted with an added wooden stick to facilitate boiling and induce crystal growth.

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New compounds containing phenylphosphine, diphenylphosphine, and methoxydiphenylphosphine were prepared by the following method. $P(OMe)Ph_2$ (0.6 ml) was added to a suspension of $(NH_4)_5[Mo_2Cl_8]Cl{\cdot}H_2O$ (0.10 g, 0.16 mmol) in methanol (10 ml) in a nitrogen-filled glove bag. The reaction mixture immediately turned greenish-blue and was then refluxed for 15 min during which a blue–green precipitate formed. The system was cooled to room temperature, then to 0 °C for 30 min, and the solid was filtered off, washed with absolute ethanol and diethyl ether, and dried under vacuum; yield 71%. *Anal.* Calc. for $MoCl_2P_2C_{26}H_{26}O_2$ $[Mo_2Cl_4(P(OMe)Ph_2)_4]$: C, 52.10; H, 4.38; Cl, 11.83. Found: C, 50.38; H, 4.16; Cl, 12.66%. Similar yields were obtained for the PH_2Ph (66%, dull green) and $PHPh_2$ (77%, bright green) reactions. *Anal.* Calc. for $MoCl_2P_2C_{12}H_{14}$-$[Mo_2Cl_4(PH_2Ph)_4]$: C, 37.24; H, 3.65; Cl, 18.32. Found: C, 35.23; H, 3.42, Cl, 18.96%. Calc. for $MoCl_2P_2C_{24}H_{22}$ $[Mo_2Cl_4(PHPh_2)_4]$: C, 53.45; H, 4.12; Cl, 13.15. Found: C, 51.28; H, 4.20; Cl, 13.48%. The previously reported deep blue compounds of the type $Mo_2Cl_4(PR_3)_4$ and incorporating trimethylphosphine, triethylphosphine, tri-n-propylphosphine, tri-n-butylphosphine, dimethylphenylphosphine, diethylphenylphosphine, methyldiphenylphosphine, ethyldiphenylphosphine, and trimethylphosphite were prepared by this method or variations of it [6–8].

For tris(2-chloroethyl)phosphite, 4-ethyl-2,6,7-trioxo-1-phosphabicyclo[2.2.2]octane, chlorodiphenylphosphine, and trivinylphosphine (PVy_3) use of $Mo_2Cl_8^{4-}$ as a reactant was unsuccessful. However, reaction of these ligands to form complexes of the type $Mo_2Cl_4(PR_3)_4$ as indicated by solution electronic spectra was accomplished with $Mo_2(O_2CCH_3)_4$ or $Mo_2(O_2CCF_3)_4$ and chlorotrimethylsilane; the following procedure is typical [9]. To a suspension of $Mo_2(O_2CCF_3)_4$ (0.050 g, 0.077 mmol) in dichloromethane (10 ml) were added Me_3SiCl (1.0 ml) and $P(OCH_2CH_2Cl)_3$ (1.0 ml). The blue–green solution was stirred at room temperature for 30 min. Although this color persists indefinitely, no solid could be recovered from this solution. With $P(OCH_2)_3CCH_2CH_3$ and $PClPh_2$ colors indicative of formation of desired complexes last only a few minutes in CH_2Cl_2 but for adequate duration to record electronic spectra. Only a small amount of a tacky blue solid could be isolated from the reaction involving PVy_3 in tetrahydrofuran.

No evidence of reaction to form $Mo_2Cl_4(PR_3)_4$ complexes was observed with tricyclohexylphosphine, triphenylphosphite, or tris(4-chlorophenyl)phosphite by either synthetic method. Reaction of tris(2-cyanoethyl)phosphine with either $Mo_2Cl_8^{4-}$ in methanol or $Mo_2(O_2CCF_3)_4/Me_3SiCl$ in THF afforded only an occasionally reproducible blue–green highly insoluble solid.

Preparation of Crystals for Structure Determinations

$Mo_2Cl_4(PEt_3)_4$. Single crystals could not be obtained from solutions of the product isolated via the above procedures. Therefore the following purification steps were performed. Silica gel (100–200 mesh) was dried overnight in an oven at 160 °C, then kept under 0.005 mm vacuum for 12 h at 120 °C. Dry, distilled THF was then used to treat the gel, and the slurry was wet-packed under Ar in a 15 × 2.0 cm column. The column was fitted with standard joints and a gas inlet to allow for air-free manipulations. The column was washed with 6:1 toluene:THF, and a toluene solution of $Mo_2Cl_4(PEt_3)_4$ was introduced. Elution with the same toluene/THF mixture separated a blue product band from some black impurities. The blue band was collected under Ar and layered with ethanol to induce crystallization. After a few hours, well-formed crystals of $Mo_2Cl_4(PEt_3)_4$ grew on the walls of the flask.

$Mo_2Cl_4(PMe_2Ph)_4$. Crystals were obtained from a toluene solution of the compound by evaporation of the solvent under a slow stream of nitrogen.

$Mo_2Cl_4(PPh_2H)_4$. Crystals were grown by slow evaporation of a CH_2Cl_2 solution under nitrogen.

X-ray Crystallographic Procedures

The data collection procedures have been described previously [10]. Important data collection parameters for $Mo_2Cl_4(PEt_3)_4$, $Mo_2Cl_4(PMe_2Ph)_4$ and $Mo_2Cl_4(PHPh_2)_4$ are given in Table I.

$Mo_2Cl_4(PEt_3)_4$. The only extinction observed in the data was that expected for the body-centering condition. Thus the centric space groups $Im3$ and $Im3m$ and the non-centric space groups $I23$, $I2_13$, $I432$, and $I\bar{4}3m$ were consistent with the absences. Refinement was begun in space group $I\bar{4}3m$ since the symmetry was consistent with that expected for the molecule. The limitation of two molecules per unit cell required that the molecular unit be located on the origin. This requirement dictated some disorder if the molecule indeed contained only two metal atoms. Similar types of disorder have been previously observed such that the ligands around a metal dimer describe a cube within which the dimetal unit has more than one possible orientation [11].

The position of the Mo atom was calculated assuming a metal–metal distance consistent with quadruply-bonded molybdenum dimers. After two cycles of isotropic refinement, a difference Fourier synthesis revealed the Cl and P atoms, although they were indistinguishable from each other. Arbitrary assignment was made, and further least-squares refinement followed by difference Fourier syntheses revealed peaks indicative of the carbon atoms around

TABLE I. Crystallographic Data Collection Parameters

	$Mo_2Cl_4(PEt_3)_4$	$Mo_2Cl_4(PMe_2Ph)_4$	$Mo_2Cl_4(PHPh_2)_4$
Formula	$Mo_2Cl_4P_4C_{24}H_{60}$	$Mo_2Cl_4P_4C_{32}H_{44}$	$Mo_2Cl_4P_4C_{48}H_{44}$
Formula weight	806.3	886.29	1078.46
Space group	$I\bar{4}3m$	$C2/c$	$P\bar{1}$
a (Å)	12.37(8)	17.868(2)	11.944(3)
b (Å)		10.049(1)	18.584(5)
c (Å)		23.952(3)	11.260(3)
α (°)			94.75(2)
β (°)		117.501(8)	106.67(2)
γ (°)			84.44(2)
V (Å^3)	1894(6)	3815(1)	2379(2)
Z	2	4	2
D_{calc} (g cm^3)	1.413	1.543	1.506
Crystal size (mm)	0.2 × 0.2 × 0.2	0.15 × 0.20 × 0.30	0.10 × 0.12 × 0.25
μ(Mo Kα) (cm^{-1})	(Cu K$_\alpha$): 99.3	7.20	6.03
Data collection instrument	Syntex P$\bar{1}$	Enraf-Nonius CAD-4	Syntex P$\bar{1}$
Radiation (monochromated in incident beam)	Cu K$_a$	Mo K$_a$	Mo K$_a$
Orientation reflections, number, range (2θ)	15, 25°–72°	25, 25°–32°	15, 20°–27°
Temperature (°C)	5 ± 1	25 ± 1	25 ± 1
Scan method	ω–2θ	ω–2θ	ω–2θ
Data collection range, 2θ (°)	5–120	4–50	4–50
No. unique data, total with $F_o^2 > 3\sigma(F_o^2)$	100	1726	3340
No. parameters refined	23	190	539
R^a	0.0480	0.0476	0.0380
$R_w{}^b$	0.0645	0.0594	0.0510
Quality of fit indicator^c	1.44	1.37	1.16
Largest shift/e.s.d., final cycle	0.34	0.01	0.01
Largest peak (e/Å^3)	0.52	0.77	0.46

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality-of-fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{parameters})]^{1/2}$.

both the Cl and P atoms. The centric groups $Im3$ and $Im3m$ impose an additional disorder in which each of the coordination sites have 50% occupancy of Cl or P, so the change was made to $Im3m$. Refinement with all five independent atoms anisotropic converged in both $Im3m$ and $Im3$, but the discrepancy factor (R) would not go below 0.08. At this point a switch back to $I\bar{4}3m$ was made, and a trial-and-error choice of Cl or the $P(C_2)_3$ unit in the two possible positions indicated the correct solution when the value of R dropped below 0.05. Refinement of the 23 parameters fit to 100 unique data gave final values of R = 0.048 and R_w = 0.065.

$Mo_2Cl_4(PMe_2Ph)_4$. The position of the Mo atom was determined by direct methods. The remaining atoms were found in a series of difference Fourier maps alternating with least-squares refinement of the atoms found. Final refinement of the 21 independent atoms with anisotropic thermal parameters converged to R = 0.048 and R_w = 0.051.

$Mo_2Cl_4(PPh_2H)_4$. The positions of the two independent Mo atoms were determined by direct methods. The remaining non-hydrogen atoms and the four phosphine hydrogen atoms were located by difference Fourier methods. Least-squares refinement using anisotropic thermal parameters for all non-hydrogen atoms gave the discrepancy factors R = 0.038 and R_w = 0.051.

Physical Measurements

Infrared spectra were recorded on a Pye Unicam SP3-300 infrared spectrophotometer by means of mineral oil mulls supported on KBr plates (4000–400 cm^{-1}) and polyethylene disks (400–200 cm^{-1}). Electronic absorption spectra were obtained using a Perkin-Elmer 330 UV/VIS/NIR spectrophotometer with solid-state spectra recorded as mulls on filter paper and solution spectra recorded with dichloromethane in 1-cm quartz cells. In some cases free phosphine had to be added to solutions to repress decomposition of the complex. Simple linear-regression

TABLE II. Positional and Isotropic Equivalent Displacement Parameters[a] and Root-Mean-Square Amplitudes of Thermal Vibration for $Mo_2Cl_4(PEt_3)_4$

Atom	x	y	z	B_{eq}	Maximum r.m.s. amplitude (A)
Mo	0.0865(4)	0.0	0.0	5.70(5)	0.283
Cl	0.1384(4)	$-x$	$-x$	10.18(7)	0.374
P	0.1403(3)	x	x	8.82(6)	0.376
C(1)	0.122(2)	x	0.281(2)	25.1(7)	0.721
C(2)	0.129(2)	x	0.369(2)	26.1(9)	0.767

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3)]$.

analysis of the electronic spectral data was accomplished with the statistical software package MINITAB (copyright Pennsylvania State University).

Results

New Structures

$Mo_2Cl_4(PEt_3)_4$. The molecular structure is qualitatively the same as that of $Re_2Cl_4(PEt_3)_4$ [11] with slight differences in bond lengths and angles, although in a different space group. The atomic positional parameters, isotropic equivalent thermal parameters, and maximum root-mean-square (r.m.s.) amplitudes of thermal vibration are given in Table II, and the molecular dimensions in Table III. The molecule is depicted in Fig. 1, in which the atom-numbering scheme is defined. The molecular dimensions appear less accurate than might be expected due to the metal atom disorder; however, the distances and angles are precise. The metal–metal bond length of 2.141(9) Å is not significantly longer than that of the PMe_3 analogue (2.130 Å [8]). The difference, if real, probably arises from the steric demands of the bulkier PEt_3 ligands, although other electronic effects might contribute, as will be discussed. The P–C(1)–C(2) bond angle of 163.0(3)° gives cause for concern, as does the C(1)–C(2) distance of 1.09(5) Å. Inspection of the maximum r.m.s. amplitudes of thermal vibration and the large thermal parameters for C(1) and C(2) reveals some degree of uncertainty in the actual positions of the carbon atoms. Since the maximum r.m.s. amplitudes are approximately perpendicular to the 8c(3m) mirror planes on which the carbon atoms are fixed, it is probable that the 'true' carbon positions are a disordered set on either side of these planes. Some disorder is required since a given Mo–P–C(1) angle cannot be simultaneously correct for all three disordered Mo atoms.

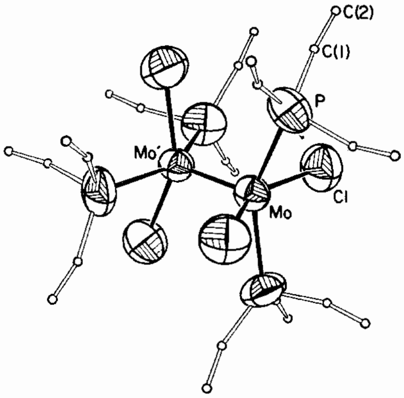

Fig. 1. ORTEP diagram of the $Mo_2Cl_4(PEt_3)_4$ molecule. Except for Mo, only the unique atoms are labeled, all others being generated by symmetry.

TABLE III. Bond Distances (A) and Bond Angles (°) for $Mo_2Cl_4(PEt_3)_4$[a]

Atoms	Distances
Mo–Mo'	2.141(9)
Mo–Cl	2.505(2)
Mo–P	2.544(5)
P–C(1)	1.77(4)
C(1)–C(2)	1.09(5)
Atoms	**Angles**
Mo'–Mo–Cl	104.8(2)
Mo'–Mo–P	105.2(2)
Cl'–Mo–Cl	150.3(3)
P'–Mo–P	149.7(4)
Cl–Mo–P	86.16(6)
Mo–P–C(1)	123.2(6)
Mo–P–C(1)'	95.0(1)
C(1)'–P–C(1)	104.0(1)
P–C(1)–C(2)	163.0(3)

[a] Numbers in parentheses are e.s.d.s in the least significant digit.

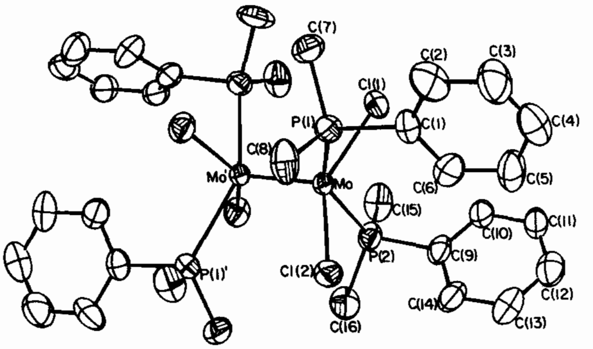

Fig. 2. ORTEP diagram of the $Mo_2Cl_4(PMe_2Ph)_4$ molecule showing the atom numbering scheme. Half of the molecule is generated by the twofold axis which bisects the metal–metal bond.

$Mo_2Cl_4(PMe_2Ph)_4$. The molecular structure is shown in Fig. 2. Atomic positional parameters and a list of bond distances and angles are presented in Tables IV and V, respectively. The structure refined smoothly with no disorder. The molecule has imposed crystallographic C_2 symmetry. The PMe_2Ph ligands are oriented so that the phenyl groups all project away from the Mo_2 unit, with the P–C bonds lying roughly parallel to the Mo–Mo axis. This then allows for a rather neat packing of the methyl groups and the Cl atoms over the Mo_2 unit.

$Mo_2Cl_4(PHPh_2)_4$. The entire molecule is the asymmetric unit. The positional parameters are listed in Table VI, selected bond distances and angles in Table VII, and the molecular structure is depicted in Fig. 3. The structure refined smoothly with no disorder. The rotational orientations of the $PHPh_2$ ligands are all similar; they direct the phenyl groups outward and place the H atoms more or less over the Mo_2 unit.

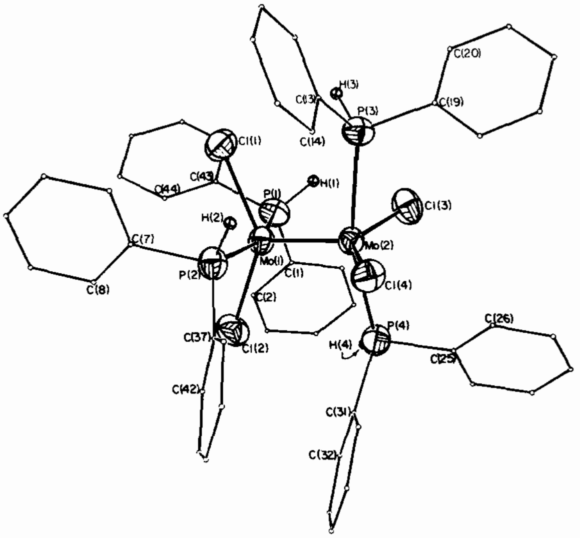

Fig. 3. ORTEP diagram of the $Mo_2Cl_4(PHPh_2)_4$ molecule. Thermal ellipsoids for the Mo, Cl and P atoms are shown at the 50% level. The carbon and hydrogen atoms are shown as arbitrarily sized uniform circles. The phenyl carbon numbering scheme follows from those given.

TABLE IV. Positional and Isotropic Equivalent Displacement Parameters[a] for $Mo_2Cl_4(PMe_2Ph)_4$

Atom	x	y	z	B_{eq}
Mo	0.44741(4)	0.52341(9)	0.70424(3)	2.26(1)
Cl(1)	0.4705(2)	0.6904(3)	0.6411(1)	3.72(6)
Cl(2)	0.3512(1)	0.3529(3)	0.7031(1)	3.50(6)
P(1)	0.4857(2)	0.3590(3)	0.6400(1)	2.92(6)
P(2)	0.3443(2)	0.6894(3)	0.7106(1)	3.23(7)
C(1)	0.4037(6)	0.362(1)	0.5578(4)	3.2(3)
C(2)	0.4203(7)	0.315(1)	0.5096(5)	5.2(3)
C(3)	0.3554(7)	0.317(1)	0.4479(5)	5.7(4)
C(4)	0.2787(7)	0.367(1)	0.4332(5)	4.8(3)
C(5)	0.2578(7)	0.414(1)	0.4797(5)	4.8(3)
C(6)	0.3222(6)	0.413(1)	0.5422(5)	4.0(3)
C(7)	0.5816(6)	0.389(1)	0.6331(4)	4.3(3)
C(8)	0.4928(7)	0.179(1)	0.6610(5)	4.4(3)
C(9)	0.2507(5)	0.676(1)	0.6338(4)	3.4(3)
C(10)	0.2397(6)	0.763(1)	0.5852(4)	4.1(3)
C(11)	0.1698(6)	0.747(1)	0.5261(4)	4.3(3)
C(12)	0.1111(6)	0.647(1)	0.5149(5)	4.6(3)
C(13)	0.1232(6)	0.560(1)	0.5631(5)	5.1(3)
C(14)	0.1914(6)	0.575(1)	0.6228(5)	4.4(3)
C(15)	0.3720(7)	0.867(1)	0.7192(5)	4.8(3)
C(16)	0.3033(6)	0.663(1)	0.7677(5)	5.6(3)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ac(\cos \text{beta})B(1,3)]$.

TABLE V. Bond Distances (Å) and Bond Angles (°) for $Mo_2Cl_4(PMe_2Ph)_4$[a]

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Mo	Mo	2.1288(8)	P(2)	C(9)	1.832(8)	C(5)	C(6)	1.40(1)
Mo	Cl(1)	2.419(3)	P(2)	C(15)	1.83(1)	C(9)	C(10)	1.40(2)
Mo	Cl(2)	2.418(3)	P(2)	C(16)	1.85(1)	C(9)	C(14)	1.40(2)
Mo	P(1)	2.557(3)	C(1)	C(2)	1.40(2)	C(10)	C(11)	1.40(1)
Mo	P(2)	2.541(3)	C(1)	C(6)	1.42(1)	C(11)	C(12)	1.39(2)
P(1)	C(1)	1.834(8)	C(2)	C(3)	1.40(1)	C(12)	C(13)	1.39(2)
P(1)	C(7)	1.82(1)	C(3)	C(4)	1.34(2)	C(13)	C(14)	1.40(1)
P(1)	C(8)	1.86(1)	C(4)	C(5)	1.41(2)			

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
Mo	Mo	Cl(1)	108.65(6)	C(1)	P(1)	C(7)	102.7(5)	C(2)	C(3)	C(4)	122.0(1)
Mo	Mo	Cl(2)	107.28(6)	C(1)	P(1)	C(8)	103.1(4)	C(3)	C(4)	C(5)	121.9(9)
Mo	Mo	P(1)	105.39(6)	C(7)	P(1)	C(8)	103.7(6)	C(4)	C(5)	C(6)	117.0(1)
Mo	Mo	P(2)	104.96(6)	Mo	P(2)	C(9)	104.0(4)	C(1)	C(6)	C(5)	121.0(1)
Cl(1)	Mo	Cl(2)	144.07(7)	Mo	P(2)	C(15)	118.6(5)	P(2)	C(9)	C(10)	120.1(7)
Cl(1)	Mo	P(1)	84.4(1)	Mo	P(2)	C(16)	119.7(4)	P(2)	C(9)	C(14)	120.2(8)
Cl(1)	Mo	P(2)	85.4(1)	C(9)	P(2)	C(15)	105.0(5)	C(10)	C(9)	C(14)	119.6(8)
Cl(2)	Mo	P(1)	85.5(1)	C(9)	P(2)	C(16)	104.0(5)	C(9)	C(10)	C(11)	119.0(1)
Cl(2)	Mo	P(2)	86.2(1)	C(15)	P(2)	C(16)	103.6(6)	C(10)	C(11)	C(12)	121.0(1)
P(1)	Mo	P(2)	149.65(7)	P(1)	C(1)	C(2)	120.8(7)	C(11)	C(12)	C(13)	119.0(8)
Mo	P(1)	C(1)	109.4(4)	P(1)	C(1)	C(6)	120.2(8)	C(12)	C(13)	C(14)	121.0(1)
Mo	P(1)	C(7)	118.1(4)	C(2)	C(1)	C(6)	119.0(8)	C(9)	C(14)	C(13)	120.0(1)
Mo	P(1)	C(8)	117.9(4)	C(1)	C(2)	C(3)	119.0(1)				

[a] Numbers in parentheses are e.s.d.s in the least significant digits.

TABLE VI. Positional and Isotropic Equivalent Displacement Parameters for $Mo_2Cl_4(PHPh_2)_4$

Atom	x	y	z	B_{eq} [a]
Mo(1)	0.22381(6)	0.26332(3)	0.15750(6)	3.05(2)
Mo(2)	0.22361(6)	0.26230(3)	0.34800(6)	3.00(2)
Cl(1)	0.0279(2)	0.2832(1)	0.0278(2)	4.34(5)
Cl(2)	0.4170(2)	0.2463(1)	0.1341(2)	4.48(5)
Cl(3)	0.2189(2)	0.3835(1)	0.4387(2)	4.56(5)
Cl(4)	0.2238(2)	0.1420(1)	0.4118(2)	3.93(5)
P(1)	0.2393(2)	0.3985(1)	0.1441(2)	3.79(5)
P(2)	0.1928(2)	0.1310(1)	0.0973(2)	3.47(5)
P(3)	0.0016(2)	0.2795(1)	0.3126(2)	3.49(5)
P(4)	0.4442(2)	0.2595(1)	0.4459(2)	3.66(5)
C(1)	0.3811(7)	0.4363(4)	0.1980(7)	4.3(2)
C(2)	0.4575(8)	0.4304(5)	0.1238(9)	6.6(3)
C(3)	0.5676(9)	0.4592(6)	0.166(1)	7.3(3)
C(4)	0.600(1)	0.4950(7)	0.280(1)	8.7(4)
C(5)	0.526(1)	0.5005(8)	0.356(1)	13.2(4)
C(6)	0.416(1)	0.4715(7)	0.313(1)	9.7(4)
C(7)	0.1438(7)	0.1161(4)	−0.0719(6)	3.7(2)
C(8)	0.2247(8)	0.1173(4)	−0.1394(7)	4.6(2)
C(9)	0.1861(9)	0.1048(5)	−0.2718(7)	5.4(2)
C(10)	0.069(1)	0.0925(5)	−0.3304(8)	6.0(3)
C(11)	−0.0093(9)	0.0940(5)	−0.2609(8)	6.0(3)
C(12)	0.0269(8)	0.1052(5)	−0.1278(7)	5.2(2)
C(13)	−0.0988(7)	0.2121(4)	0.2300(7)	3.9(2)
C(14)	−0.0659(7)	0.1399(4)	0.2443(8)	4.5(2)
C(15)	−0.1458(8)	0.0875(5)	0.1799(8)	5.6(3)
C(16)	−0.2557(9)	0.1100(5)	0.1059(9)	6.3(3)
C(17)	−0.2884(9)	0.1836(6)	0.092(1)	7.9(3)
C(18)	−0.2093(9)	0.2345(5)	0.1550(9)	6.4(3)
C(19)	−0.0435(7)	0.3033(4)	0.4527(7)	4.0(2)
C(20)	−0.1268(8)	0.3617(5)	0.4539(9)	6.2(3)
C(21)	−0.1624(9)	0.3794(6)	0.563(1)	7.9(3)
C(22)	−0.1139(9)	0.3396(5)	0.6670(9)	6.8(3)
C(23)	−0.0314(9)	0.2818(5)	0.6644(8)	6.1(3)
C(24)	0.0076(8)	0.2639(4)	0.5595(7)	4.7(2)
C(25)	0.4805(7)	0.2806(5)	0.6129(7)	4.5(2)
C(26)	0.4085(9)	0.2614(5)	0.6803(8)	6.1(3)
C(27)	0.441(1)	0.2749(6)	0.8096(8)	7.2(3)
C(28)	0.537(1)	0.3081(6)	0.8690(9)	7.8(3)
C(29)	0.608(1)	0.3278(9)	0.804(1)	14.1(5)
C(30)	0.580(1)	0.3129(8)	0.672(1)	11.5(4)
C(31)	0.5517(7)	0.1833(4)	0.4398(6)	3.7(2)
C(32)	0.6622(7)	0.1954(5)	0.4290(9)	5.8(3)
C(33)	0.7485(9)	0.1390(6)	0.438(1)	7.4(3)
C(34)	0.7251(9)	0.0698(5)	0.4569(8)	5.7(3)
C(35)	0.6147(9)	0.0577(5)	0.469(1)	6.6(3)
C(36)	0.5275(9)	0.1145(5)	0.4606(9)	6.3(3)
C(37)	0.2994(7)	0.0543(4)	0.1468(6)	4.0(2)
C(38)	0.261(1)	−0.0071(4)	0.1819(8)	6.2(3)
C(39)	0.345(1)	−0.0677(5)	0.2154(9)	7.5(3)
C(40)	0.455(1)	−0.0666(5)	0.2035(8)	6.3(3)
C(41)	0.4949(9)	−0.0053(5)	0.1730(9)	6.5(3)
C(42)	0.4130(8)	0.0564(5)	0.1411(8)	5.2(2)
C(43)	0.1831(7)	0.4298(4)	−0.0126(8)	4.5(2)
C(44)	0.1966(9)	0.3856(5)	−0.1116(8)	6.1(3)
C(45)	0.159(1)	0.4111(6)	−0.2338(9)	9.0(3)
C(46)	0.1012(9)	0.4814(7)	−0.248(1)	11.4(3)
C(47)	0.088(1)	0.5240(6)	−0.147(1)	11.6(3)
C(48)	0.1315(9)	0.5013(5)	−0.024(1)	7.9(3)

(continued)

TABLE VI. *(continued)*

Atom	x	y	z	B_{eq}[a]
H(1)	0.190(5)	0.440(3)	0.211(5)	3(1)*
H(2)	0.098(5)	0.113(3)	0.123(5)	3(1)*
H(3)	−0.053(5)	0.336(3)	0.242(5)	3(2)*
H(4)	0.491(5)	0.311(3)	0.419(5)	2(1)*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab\,(\cos \text{gamma})B(1,2) + ac\,(\cos \text{beta})B(1,3) + bc\,(\cos \text{alpha})B(2,3)]$.

Preparation and Characterization of Complexes

In our attempt to synthesize a series of twenty compounds of the type $Mo_2Cl_4(PR_3)_4$ we found that the reactivities of the phosphines and phosphites varied considerably. By far the majority of complexes were readily isolated by the well-established reaction with $Mo_2Cl_8^{4-}$ in alcohol solvent. Although similar results were not observed with $P(OCH_2CH_2Cl)_3$, $P(OCH_2)_3CCH_2CH_3$ and $PClPh_2$, reaction of these ligands with $Mo_2(O_2CCH_3)_4$ or $Mo_2(O_2CCF_3)_4$ and Me_2SiCl presumably yields the desired complexes as judged by the appearance of a $\delta \rightarrow \delta^*$ band in the visible spectrum. We believe our inability to recover solid materials from these solutions, which with the exception of $P(OCH_2CH_2Cl)_3$ decompose quickly in the preparative medium, is due to electronic factors to be discussed subsequently. Under no conditions did we note $Mo_2Cl_4(PR_3)_4$ formation with $P(OPh)_3$, $P(OPh\text{-}4\text{-}Cl)_3$ or PCy_3. In the case of the phosphites we again attribute this result to electronic constraints. On the other hand failure to form a tetraphosphine complex with PCy_3 is likely to be due to steric congestion accompanying coordination of two PR_3 donors to each Mo atom. The estimated cone angle [12] for PCy_3 is 170°; this value substantially exceeds that of PPh_3 (145°), a ligand for which only $Mo_2Cl_4(PPh_3)_2(MeOH)_2$ has been isolated under these conditions [13]. Finally $P(CH_2CH_2CN)_3$ and PVy_3 afforded irreproducible solid products.

Structural Results

This study began with the objective of finding correlations between the π-acceptor capacities of the PR_3 ligands and two aspects of the Mo–Mo quadruple bond: the bond length and the $\delta \rightarrow \delta^*$ transition energy. Unfortunately, the structural side of this investigation was abortive owing to the persistent difficulties in obtaining suitably crystalline compounds. Only three new crystal structures were obtained, namely, those of the compounds containing PEt_3, PMe_2Ph and $PHPh_2$. The compound with PMe_3 was structurally characterized earlier [8]. The structures of these four compounds are similar. In each case the $Mo_2Cl_4P_4$ core has effectively D_{2d} symmetry. All of the Mo–P distances are in the range 2.545 ± 0.15 Å; all of the Mo–Cl distances are in the range 2.45 ± 0.06 Å; the Mo–Mo–P and Mo–Mo–Cl angles are within the respective ranges 101.5 ± 4.0° and 108.6 ± 4.0°. Average values for individual compounds are listed in Table VIII.

Our hope of finding a correlation between the Mo–Mo distances and the electronic character of the PR_3 ligand, even over this limited group of compounds also remains unfulfilled, owing to the very small range of distances observed. While there are statistically significant differences between some of these distances according to the calculated e.s.d.s, the differences are too small to be chemically significant in view of the probable importance of steric and packing forces, of which the e.s.d.s take no account. In any event, a plot of the Mo–Mo distances against the electronic parameter for the PR_3 ligands (see below) shows no correlation whatever. We therefore concentrate our main attention on the $\delta \rightarrow \delta^*$ transitions for the various $Mo_2Cl_4(PR_3)_4$ compounds.

Infrared Spectra

Spectra in the range 4000–200 cm^{-1} were recorded on all materials isolated in the solid state and low-frequency bands (400–200 cm^{-1}) for the new compounds and those for which no previous report could be found are presented in Table IX. Published spectral data for the remaining complexes were used to verify the identities for those species. Although we and others have used the low-frequency region for structural correlations for $Mo_2Cl_4(PR_3)_4$ and $Mo_2Cl_4(PP)_2$ species, the general complexity of the spectra obtained for the present study precludes any simple analysis [14, 15].

Electronic Spectra

Electronic absorption spectra were recorded in solution for sixteen phosphines and phosphites and in the solid state for thirteen of these ligands; the results are presented in Table IX. For $P(OCH_2CH_2Cl)_3$, $P(OCH_2)_3CCH_2CH_3$, $PClPh_2$ and PVy_3 spectra were run on preparative solutions while the solutions of $P(OMe)_3$ and $P(OMe)Ph_2$ required addition of phosphite to repress decomposition of the complex. Presumably the decomposition products in these

TABLE VII. Selected Bond Distances (A) and Bond Angles (°) for $Mo_2Cl_4(PHPh_2)_4$[a]

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Mo(1)	Mo(2)	2.1474(9)	P(1)	Mo(1)	2.556(2)	P(3)	H(3)	1.37(6)
Mo(1)	Cl(1)	2.388(2)	P(1)	H(1)	1.25(6)	P(3)	C(13)	1.825(8)
Mo(1)	Cl(2)	2.385(2)	P(1)	C(1)	1.817(9)	P(3)	C(19)	1.816(9)
Mo(1)	P(1)	2.556(2)	P(1)	C(43)	1.821(9)	P(4)	Mo(2)	2.545(2)
Mo(1)	P(2)	2.530(2)	P(2)	Mo(1)	2.530(2)	P(4)	H(4)	1.25(6)
Mo(2)	Cl(3)	2.397(2)	P(2)	H(2)	1.32(7)	P(4)	C(25)	1.823(8)
Mo(2)	Cl(4)	2.404(2)	P(2)	C(7)	1.831(7)	P(4)	C(31)	1.829(8)
Mo(2)	P(3)	2.558(2)	P(2)	C(37)	1.826(8)			
Mo(2)	P(4)	2.545(2)	P(3)	Mo(2)	2.558(2)			

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
Mo(2)	Mo(1)	Cl(1)	110.06(7)	Cl(3)	Mo(2)	P(3)	83.43(7)	H(2)	P(2)	C(37)	103.0(2)
Mo(2)	Mo(1)	Cl(2)	112.18(6)	Cl(3)	Mo(2)	P(4)	85.49(7)	C(7)	P(2)	C(37)	103.6(3)
Mo(2)	Mo(1)	P(1)	99.80(6)	Cl(4)	Mo(2)	P(3)	89.82(7)	Mo(2)	P(3)	H(3)	115.0(3)
Mo(2)	Mo(1)	P(2)	97.86(6)	Cl(4)	Mo(2)	P(4)	89.93(7)	Mo(2)	P(3)	C(13)	123.4(3)
Cl(1)	Mo(1)	Cl(2)	137.76(8)	P(3)	Mo(2)	P(4)	163.41(7)	Mo(2)	P(3)	C(19)	114.4(2)
Cl(1)	Mo(1)	P(1)	85.91(7)	Mo(1)	P(1)	H(1)	115.0(3)	H(3)	P(3)	C(13)	97.0(2)
Cl(1)	Mo(1)	P(2)	84.23(7)	Mo(1)	P(1)	C(1)	120.2(3)	H(3)	P(3)	C(19)	101.0(3)
Cl(2)	Mo(1)	P(1)	86.29(8)	Mo(1)	P(1)	C(43)	114.0(3)	C(13)	P(3)	C(19)	103.4(4)
Cl(2)	Mo(1)	P(2)	90.85(8)	H(1)	P(1)	C(1)	97.0(3)	Mo(2)	P(4)	H(4)	114.0(2)
P(1)	Mo(1)	P(2)	161.88(7)	H(1)	P(1)	C(43)	106.0(2)	Mo(2)	P(4)	C(25)	111.6(3)
Mo(1)	Mo(2)	Cl(3)	110.28(6)	C(1)	P(1)	C(43)	102.2(4)	Mo(2)	P(4)	C(31)	126.8(3)
Mo(1)	Mo(2)	Cl(4)	112.58(6)	Mo(1)	P(2)	H(2)	111.0(2)	H(4)	P(4)	C(25)	97.0(2)
Mo(1)	Mo(2)	P(3)	97.57(5)	Mo(1)	P(2)	C(7)	110.5(2)	H(4)	P(4)	C(31)	102.0(3)
Mo(1)	Mo(2)	P(4)	97.83(6)	Mo(1)	P(2)	C(37)	126.4(3)	C(25)	P(4)	C(31)	100.4(3)
Cl(3)	Mo(2)	Cl(4)	137.12(8)	H(2)	P(2)	C(7)	98.0(2)				

[a] Numbers in parentheses are e.s.d.s in the least significant digits.

TABLE VIII. Comparison of Major Molecular Dimensions for some $Mo_2Cl_4(PR_3)_4$ Complexes

	PR_3			
	PEt_3	PMe_3 [a]	PMe_2Ph	$PHPh_2$
Bond lengths (Å)				
Mo–Mo	2.141(9)	2.130(0)	2.129(1)	2.147(1)
Mo–Cl	2.505(2)	2.414(1) [b]	2.418(1)	2.394(9) [c]
Mo–P	2.544(5)	2.545(1) [b]	2.549(5)	2.55(1) [c]
Bond angles (°)				
Mo–Mo–P	105.2(2)	102.3(1) [b]	105.2(2)	98.0(1) [c]
Mo–Mo–Cl	104.8(2)	112.2(2) [b]	108.0(7)	111.0(1) [c]

[a] From ref. 8. [b] Average of two similar values. [c] Average of four similar values.

TABLE IX. Spectral Properties of $Mo_2Cl_4(PR_3)_4$ Complexes [a]

PR_3	Electronic spectra (nm) [b]		Infrared spectra (cm^{-1}) [e]
	Solution [c,d]	Solid state	
PMe_3	582 (3830), 441 (280), 329 (4240)	585s, 441m, 332s	346, 324m, 279m
PEt_3	588 (2200), 448sh	588s, 458w, 403vw, 331s	
PPr^n_3	587 (1960), 453 (350)	586s, 454sh/w, 400sh/vw, 328s	
PBu^n_3	587 (1980), 440 (310)	588s, 457w, 328s	
PH_2Ph	600 (2650), 433 (790)	596s, 427s	341m, 314m-w, 293m-w, 279m, 274sh/m, 254w
PMe_2Ph	593 (3630), 430 (460)	596s, 449m, 390sh/w, 334s	387m, 352m-w, 323sh/m, 314m, 267m-w
PEt_2Ph	594 (2780), 463sh/w, 414sh/w	595s, 462m, 401sh/w, 343s	
$PHPh_2$	612 (2440), 448 (770), 424 (780)	614s, 444s	334m, 284s, 273sh/m, 204w
$PMePh_2$	600 (2570), 471 (230), 420 (270)	598s, 462sh/m, 417m, 342s	
$PEtPh_2$	596 (1960), 482sh/w, 423sh/w	600s, 487sh/w, 425sh/m, 342s	
$P(OMe)_3$	609 (2880), 443 (330), 328 (3810)	604s, 448m, 330s	
$P(OMe)Ph_2$	608 (940), 470 (280)	600s, 464m, 435sh/w	315m-s, 268m-s
PVy_3	601s, 460sh/w		
$P(OCH_2CH_2Cl)_3$	613s, 448w		
$P(OCH_2)_3CCH_2CH_3$	618s, 450w		
$PClPh_2$	620m-s, 449s		
$P(CH_2CH_2CN)_3$		613m, 461m	

[a] All solid-state spectra recorded as mineral oil mulls. [b] ±1 nm. [c] All solution spectra recorded in dichloromethane except for PVy_3 (tetrahydrofuran). [d] Molar absorptivities (M^{-1} cm^{-1}) in parentheses. [e] ±2 cm^{-1}.

cases are the tetranuclear complexes $Mo_4Cl_8(PR_3)_4$ formed by cycloaddition of two $Mo_2Cl_4(PR_3)_4$ species with loss of four PR_3 ligands, and the presence of excess PR_3 would be expected to inhibit this reaction. Evidence for this assertion comes from the growth of an intense absorption in the range 400–450 nm as the solutions decompose. McCarley and coworkers, who systematically prepared a series of these Mo_4 compounds, reported a band at 435 nm ($\epsilon = 3.5 \times 10^3$ M^{-1} cm^{-1}) for $Mo_4Cl_8(PBu^n_3)_4$ in dichloromethane [9].

To see whether the $\delta \rightarrow \delta^*$ transition energies (TEs) are correlated with the π acidities of the various PR_3 ligands, measures of the latter property are required. Two such measures are available in the literature: (1) the ^{13}C NMR chemical shift difference ($\Delta\delta(CO)$) for $Ni(CO)_4$ *versus* $Ni(CO)_3(PR_3)$ [16], and (2) the frequency of the A^1 CO stretching mode ($\bar{\nu}(CO)$) of the $Ni(CO)_3(PR_3)$ compounds [12]. The monodentate phosphines selected for our study provide a substantial range of both of these parameters. Moreover, these values for the chosen phosphines are

TABLE X. Organometallic Spectral Parameters and $\delta \rightarrow \delta^*$ Transition Energies

Phosphine	$\Delta\delta$(CO) (ppm)[a]	ν(CO) (cm^{-1})[b]	$\delta \rightarrow \delta^*$ TE (solution, $\times 10^{-3}$ cm^{-1})	$\delta \rightarrow \delta^*$ TE (solid, $\times 10^{-3}$ cm^{-1})
PMe_3	5.05	2064.1	17.18	17.09
PEt_3	5.54	2061.7	17.01	17.01
$PPr^n{}_3$	5.62		17.04	17.07
$PBu^n{}_3$	5.69	2060.3	17.04	17.01
PH_2Ph	3.54	2077.0	16.67	16.78
PMe_2Ph	4.76	2065.3	16.86	16.78
PEt_2Ph	5.36	2063.7	16.84	16.81
$PHPh_2$	3.93	2073.3	16.34	16.29
$PMePh_2$	4.53	2067.0	16.67	16.72
$PEtPh_2$	4.78	2066.7	16.78	16.67
$P(OMe)_3$	3.18	2079.5	16.42	16.56
$P(OMe)Ph_2$	3.96	2072.0	16.45	16.67
PVy_3	4.22	2069.5	16.64	
$P(OCH_2CH_2Cl)_3$	2.76	2084.0	16.31	
$P(OCH_2)_3CCH_2CH_3$	2.60	2086.8	16.18	
$PClPh_2$	2.49	2080.7	16.13	
$P(CH_2CH_2CN)_3$	3.47	2077.9		16.31[c]
PCy_3	6.32	2056.4		
$P(OPh)_3$	1.69	2085.3		
$P(OPh\text{-}4\text{-}Cl)_3$	1.32	2089.3		

[a] Ref. 16. [b] Ref. 12. [c] Not included in statistical treatment.

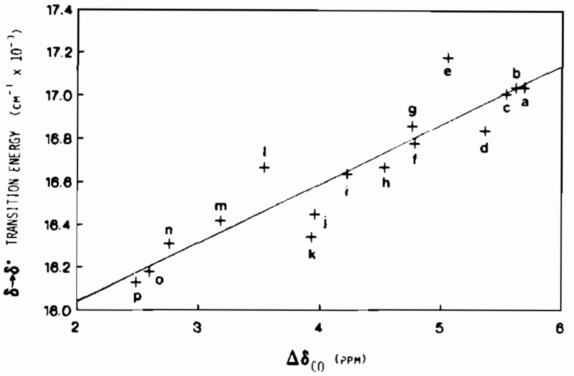

Fig. 4. Plot of $\Delta\delta$(CO) *vs.* $\delta \rightarrow \delta^*$ transition energy (solution): a, $PBu^n{}_3$; b, $PPr^n{}_3$; c, PEt_3; d, PEt_2Ph; e, PMe_3; f, $PEtPh_2$; g, PMe_2Ph; h, $PMePh_2$; i, PVy_3; j, $P(OMe)Ph_2$; k, $PHPh_2$; l, PH_2Ph; m, $P(OMe)_3$; n, $P(OCH_2CH_2Cl)_3$; o, $P(OCH_2)_3CCH_2CH_3$; p, $PClPh_2$.

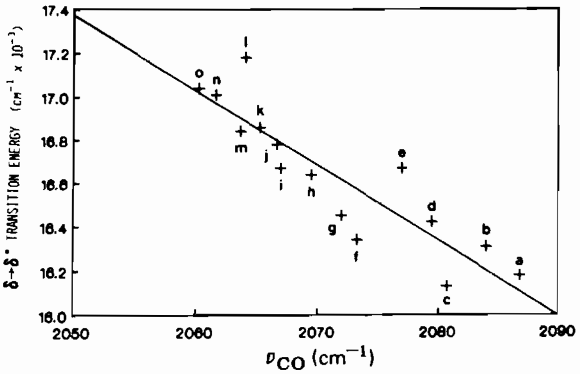

Fig. 5. Plot of $\bar{\nu}$(CO) *vs.* $\delta \rightarrow \delta$ transition energy (solution): a, $P(OCH_2)_3CCH_2CH_3$; b, $P(OCH_2CH_2Cl)_3$; c, $PClPh_2$; d, $P(OMe)_3$; e, PH_2Ph; f, $PHPh_2$; g, $P(OMe)Ph_2$; h, PVy_3; i, $PMePh_2$; j, $PEtPh_2$; k, PMe_2Ph; l, PMe_3; m, PEt_2Ph; n, PEt_3; o, $PBu^n{}_3$.

themselves highly correlated (correlation coefficient = −0.981) although there is some slight scatter in the high IR/low NMR range.

The values of $\Delta\delta$(CO), $\bar{\nu}$(CO), TE (solution) and TE (solid state) appear in Table X. The plots of $\Delta\delta$(CO) and $\bar{\nu}$(CO) *versus* TE (solution) are shown in Figs. 4 and 5. Of the two phases the solution spectral data yield a better linear correlation of $\delta \rightarrow \delta^*$ TE with the CO spectral values. Moreover, for the solution measurement the $\Delta\delta$(CO) plot gives the better linear fit. Three points fall substantially off the line and are due to PMe_3, PH_2Ph and $PHPh_2$. Inclusion of these phosphines gives a linear correlation of 0.923 whereas their exclusion yields a fit of 0.982. There is appreciably more scatter in the $\bar{\nu}$(CO) plot (−0.892 for 15 data points; no $\bar{\nu}$(CO) was reported for $PPr^n{}_3$) which is due in part to variation in the ordering of $\Delta\delta$(CO) and $\bar{\nu}$(CO) for $PClPh_2$ ($\Delta\delta$(CO) = 2.49 ppm; $\bar{\nu}$(CO) = 2080.7 cm^{-1}), $P(OCH_2)_3CCH_2CH_3$ (2.60, 2086.8), and $P(OCH_2CH_2Cl)_3$ (2.76, 2084.0).

The correlation between the $\delta \rightarrow \delta^*$ TE and the π-acidity parameters suggests that as the electron withdrawing ability of the phosphine increases, the energy gap between δ and δ^* orbitals decreases with concomitant weakening of the δ bond. However, electron correlation and relaxation effects may cause the actual energy difference to be less than the $\delta \rightarrow \delta^*$ TE [17]. It is difficult to assess the relative contribution of the latter effects across the present series of complexes. Presumably, weakening of the δ component accompanies withdrawal of electron density from this orbital into $d\pi$ orbitals on the phosphorus atom. Thus the electron-releasing alkyl substituents lead to the highest energy transitions in the series, chlorine and alkoxy groups result in the lowest, and hydrogen and phenyl fall in the midrange. The plot of $\delta \rightarrow \delta^*$ TE *versus* $\Delta\delta(CO)$ would appear to be the more useful as a predictive tool in that the existence or relative stability of $Mo_2Cl_4(PR_3)_4$ species can be assessed. Hence, the complexes occurring only in the preparative media incorporate phosphines (PVy_3 excepted) for which $2.0 < \Delta\delta(CO) < 2.5$ ppm, and for $P(OPh)_3$ and $P(OPh\text{-}4\text{-}Cl)_3$, which have $\Delta\delta(CO) < 2.0$, no such complex formation occurs. The ability of strongly π-acid ligands such as isocyanides to cleave the Mo–Mo bond in $Mo_2Cl_4(PR_3)_4$ has been amply documented, and the phenyl phosphites may be presumed to behave similarly [18]. Also we note that those phosphines for which dimerization readily occurs are those again with relatively low $\Delta\delta(CO)$ values.

No simple explanation presents itself for the off-line behavior of PMe_3, PH_2Ph and $PHPh_2$ solution TE data, but we note that each of these ligands involves small substituents, either hydrogen atoms or three methyl groups. Although emission studies on $M_2Cl_8^{n-}$ (M = Mo, Re) indicate that the $^1(\delta\delta^*)$ excited state exhibits a staggered configuration about the M–M bond, the emission properties of $Mo_2Cl_4(PR_3)_4$ (R = Et, Pr^n, Bu^n) suggest a retention of an eclipsed array in this excited state due to the bulk of the R groups [19, 20]. Yet the emission lifetime and quantum yield for $Mo_2Cl_4(PMe_3)_4$ differ substantially from the values for the other PR_3 complexes, indicative of unique behavior for the smaller PMe_3 ligand.

The solid state plots of $\delta \rightarrow \delta^*$ TE *versus* the organometallic spectral parameters show only a general trend of increasing TE with increasing $\Delta\delta(CO)$ (0.740) and decreasing TE with increasing $\bar{\nu}(CO)$ (−0.688). We note also that plots of both solid state and solution TE *versus* Mo–Mo bond length for the four structurally characterized $Mo_2Cl_4(PR_3)_4$ complexes revealed no correlation pattern whatsoever. These observations suggest that additional factors must be considered in understanding the electronic structures of the materials in the solid state.

The results of this work can be compared with the results of a recent examination of the series of compounds $Mo_2X_4(PMe_3)_4$ with X = Cl, Br and I [21]. Here it was also found that the Mo–Mo distance is insensitive to the ligand changes, whereas the $\delta \rightarrow \delta^*$ transition responds markedly. In this study the Mo–Mo stretching frequencies were also measured and showed a moderate response.

Supplementary Material

Tables of structure factors, anisotropic thermal parameters and complete lists of bond distances and angles are available from author F.A.C.

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