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Trigonal-Bipyramidal *vs.* Tetragonal-Pyramidal Geometry in [Mo(η^5-C$_5$H$_5$)CH$_3$(CO)diphos] Complexes

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UV irradiation of THF solutions containing equimolar amounts of [Mo(Cp)CH$_3$(CO)$_3$] (Cp = η^5-C$_5$H$_5$) and a bidentate phosphine ligand LL yields as the main component [Mo(Cp)CH$_3$(CO)LL], which can be isolated by precipitation with heptane. This reaction path, which has been investigated for monodentate phosphines such as PMe$_3$ [1], PPh$_3$ [2] and P(OPh)$_3$ [3], is to be expected for a photo-induced substitution with CO elimination as the primary step [4]. In polymer matrices, the favoured primary step is the fission of the molybdenum–methyl bond [5]; CH$_3$-free, dinuclear complexes [Mo(Cp)(CO)L$_2${Mo(Cp)(CO)$_3$}] have also been observed as by-products in photo-reactions carried out in solution (L, *e.g.*, PMe$_3$ [1]). More rigorous experimental conditions can generate hydrido complexes such as [Mo(Cp)H(CO)$_2$P(OPh)$_3$] [3] and [Mo(Cp)H(CO)PPh(OCH$_2$CH$_2$)$_2$NH] [6], and the ionic species [Mo(Cp)(CO)$_2$LL][Mo(Cp)(CO)$_3$] [7].

We have recently reported on first investigations into the systems [Mo(Cp)CH$_3$(CO)LL], where LL = *cis*-Ph$_2$PCH=CHPPh$_2$ (c-dpe), 1,2-C$_6$H$_4$(PPh$_2$)$_2$ and 1,2-C$_6$H$_4$AsPh$_2$(PPh$_2$) [8]. Interpretation of the ^{31}P NMR spectra leads to the conclusion that solutions of these complexes should contain species with trigonal-bipyramidal geometry (the cyclopentadienyl ligand is considered here as a simple axial ligand). In the present work we present further evidence for trigonal geometry for complexes with LL = Ph$_2$PCH$_2$PPh$_2$ (dppm), Ph$_2$P(CH$_2$)$_3$PPh$_2$ (dppp), Ph$_2$As(CH$_2$)$_2$PPh$_2$ (arphos) and c-dpe, based on ^{1}H (Cp and CH$_3$ region) and ^{31}P NMR spectroscopic characteristics. c-Dpe, due to its unsaturated carbon back-bone, forms chelate-5 rings which are substantially rigid. With dppm *trans* positions for the two phosphorus functions in a potential tetragonal {Mo(CH$_3$)(CO)LL} unit, such as postulated from the observation of two ^{1}H(Cp) signals for LL = Me$_2$P(CH$_2$)$_2$PMe$_2$ [9], can be excluded. Arphos should give rise to particularly simple spectra (lacking ^{31}P–^{31}P coupling).

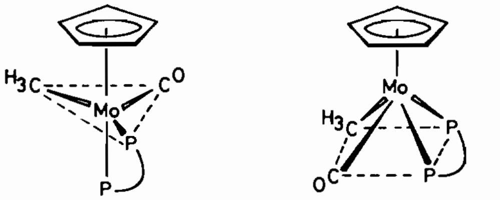

Fig. 1. Trigonal-bipyramidal and tetragonal-pyramidal structures for the complexes [Mo(Cp)CH$_3$(CO)diphos], taking into account the inequivalency of the two phosphorus functions. The tetragonal ligand arrangement of [M(Cp)L$_4$] complexes is, according to theoretical considerations carried out by R. Hoffmann, the energetically preferred one [15] and has been established for complexes containing monodentate phosphines by, *inter alias*, ^{1}H [1] and ^{13}C NMR spectroscopy [16].

Spectroscopic data, including those of selected compounds from the literature, are collated in Table I. The size of the ^{1}H–^{31}P coupling constants is a valuable indicator for the ligand arrangement in these complexes. Thus, coupling constants J(P–CH$_3$)$_{cis}$ are around 12, J(P–CH$_3$)$_{trans}$ around 2–3 Hz, and J(P–Cp) is *ca.* 1.5 Hz. No P–Cp coupling is observed in the complexes [Mo(Cp)CH$_3$(CO)$_2$PR$_3$] if the phosphine is *cis* to the methyl ligand; nonetheless, the Cp signal in [Mo(Cp)CH$_3$(CO)(PMe$_3$)$_2$] where the two phosphines reportedly are *cis* to CH$_3$, is a triplet [1]. ^{1}H shielding increases with increasing CO substitution and is greater in *trans*- than in *cis*-[Mo(Cp)CH$_3$(CO)$_2$PMe$_3$].

The most intriguing aspect with the spectra of our bis(phosphine) complexes is the fact that there are two distinctly separate ^{31}P resonances. Hence, contrasting with [Mo(Cp)CH$_3$(CO)(PMe$_3$)$_2$], the P atoms are not equivalent, and there is only one possible ligand arrangement in a tetragonal or trigonal geometry (Fig. 1). Further, the cyclopentadienyl signals appear as doublets. In a tetragonal-pyramidal ligand arrangement, the two phosphorus atoms should couple in an approximately equivalent manner with the Cp protons, giving rise to a doublet of doublets (or, in limiting cases, a triplet). In addition, the Cp signals as compared with those of analogous complexes (Table I) are shifted substantially to lower frequencies (higher magnetic field). These findings can be interpreted in terms of a trigonal-bipyramidal ligand arrangement with one phosphorus function in the equatorial plane coupling to the Cp protons, and the other P in the more distant axial position where coupling to Cp is below the limit of resolution. It has been shown, in phosphine derivatives of [Fe(CO)$_5$] that the coupling constants J(^{31}P–^{13}CO) decrease with decreasing involvement of couplings of equatorial CO groups: [Fe(CO)$_3$(PEt$_3$)$_2$] (3 CO$_{eq}$) = 28 [10]; [Fe(CO)$_2$(PMe$_3$)$_2$L] (2 CO$_{eq}$) = 24 and

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TABLE I. Spectroscopic Data of Phosphine Derivatives of [Mo(Cp)$CH_3(CO)_3$].[a]

Complex	ν(CO)[b] (cm^{-1})	$\delta(^1H)_{Cp}$[c] (ppm)	$\delta(^1H)_{Me}$[c] (ppm)	$\delta(^{31}P)$[d] (ppm)	Lit.
[Mo(Cp)Me(CO)dppm]	1820	4.68(d, 1.3)	0.32(d, 2.3)	35.6/25.9(53.2), 310 K	e
		[4.55(m)]		[64.4/−25.5[f] (70[j])]	
[Mo(Cp)Me(CO)arphos]	1830	4.38(d, 1.2)	−0.13(d, 2.4)	98.3, 300 K; 97.8, 210 K	e
		[4.18, 4.39]	[−0.16, −0.28]	[95.1, 94.3]	
[Mo(Cp)Me(CO)c-dpe]	1850	4.06(d, 1.8)	−0.12(dd, 10.3/1.8)	102.8/96.4 (11.8), 300 and 210 K	e
	[1955, 1912, 1896,	[4.33(d, 1.2[g]]	[0.01]	[99.8/84.2 (18), 300 K;	
	1782, 1763]			[101.8/83.6 (18), 210 K]	
[Mo(Cp)Me(CO)dppp]	1805	4.67(d, 1.5)	−0.22(m)[h]	53.8/51.2, 210 K	e
	[1955, 1930, 1815]	[5,16, 5.52; 4.27(m)]		[72.0/−17.6[f]; 47.7(17.7), 210 K]	
[Mo(Cp)Me(CO)$(PMe_3)_2$]	1787	4.89(t, 0.8)	−0.62(t, 12.8)	35.1	1
cis-[Mo(Cp)Me$(CO)_2PMe_3$]	1944, 1938, 1858	5.16	−0.13(d, 11.8)	23.4	1
trans-[Mo(Cp)Me$(CO)_2PMe_3$]		4.96(d, 1.6)	0.16(d, 2.8)	25.6	1
[Mo(Cp)Me$(CO)_2PPh_3$]	1940, 1850	4.70(d, 2)			2
cis-[Mo(Cp)Me$(CO)_2P(OPh)_3$]	1961, 1880	4.70	0.29(d, 11)		3
trans-[Mo(Cp)Me$(CO)_2P(OPh)_3$]	1968, 1886	4.51(d, 1.2)	0.30(d, 3)		3
[Mo(Cp)Me$(CO)_3$]	2022, 1930	5.37	0.33		e
[Mo(Cp)CO$(PMe_3)_2${Mo(Cp)$(CO)_3$}]	1956, 1894, 1874	5.67(t, 1.2); 4.97		35.1	1
[Mo(Cp)$(CO)_2PPh(OR)_2$]$^+$	1990, 1900	6.0		198	6
[Mo(Cp)H$(CO)_2PPh(OR)_2$]	1945, 1860	5.26, 5.13	i	200	6

[a] Abbreviations: Cp = η^5-C_5H_5, Me = CH_3, Ph = C_6H_5, dppm = $Ph_2PCH_2PPh_2$, arphos = $Ph_2As(CH_2)_2PPh_2$, c-dpe = *cis*-$Ph_2PCH{=}CHPPh_2$, dppp = $Ph_2P(CH_2)_3PPh_2$, $PPh(OR)_2$ = $PhP(OCH_2CH_2)_2NH$. Signals for by-products are given in square brackets. All data are for THF solutions (except of $\delta(^{31}P)$ for [Mo(Cp)CH_3(CO)dppm] in toluene) and at room temperature unless indicated otherwise ($\delta(^{31}P)$ values. [b] For phases, see key references. [c] 80 MHz; coupling pattern and coupling constants are given in parentheses: d = doublet, dd = doublet of doublets, t = triplet, m = poorly resolved or multiplet. [d] {^1H}, 36.44 MHz; coupling constants [$^2J(^{31}P-^{31}P)$ for dppm, $^3J(^{31}P-^{31}P)$ for c-dpe] are in parentheses; throughout, doublets are observed. [e] This work. [f] The ligand is coordinated with only one of its Ph_2P groups. [g] No methyl group present. [h] See text for discussion. [i] $\delta(^1H)$ for the hydride ligand is −6.41(65) and −6.23(23) Hz (ppm). [j] The four components of the two doublets show a fine-structure splitting of 6 Hz.

19 [11]; $[Fe(CO)_4PEt_3]$ ($3\ CO_{eq} + 1\ CO_{ax}$) = 19 [12]; $[Fe(CO)_3Me_2P(CH_2)_2PMe_2]$ ($2\ CO_{eq} + 1\ CO_{ax}$) = 6.9 Hz [13].

Coupling pattern and position of the methyl protons do not allow for an unambiguous distinction between the two structure types (Fig. 1), if one assumes that $J(P_{ax}-CH_3)$ in trigonal-bipyramidal complexes is of the same order of magnitude as $J(P-CH_3)_{trans}$, namely around 2 Hz. The c-dpe complex shows the coupling pattern expected for the A part of an A_3XY spin system [$X = P_{eq}$ (or P_{cis}), $Y = P_{ax}$ (or P_{trans})], *i.e.* a doublet of doublets with J(AX) = 10.3 and J(AY) = 1.8 Hz. For dppp the signal (centered at –0.22 ppm) is basically a doublet of doublets (J *ca.* 8 and 4 Hz), though poorly resolved. In the dppm complex, the methyl protons exhibit a doublet of J(HP) = 2.3 Hz despite the fact that two non-equivalent P atoms are present. The reduction of coupling interaction relative to that observed with the c-dpe complex may be a consequence of disturbed overlap due to angle distortions in the strained chelate-4 ring (for discussion of this phenomenon see ref. 14). Finally, in the arphos complex, there are two weak singlets (–0.16 and –0.28 ppm) which probably correspond to Ph_2As coordinated species, and a doublet (main signal at –0.13 ppm) of J(HP) = 2.4 Hz. The corresponding Cp resonance at 4.38 ppm is a doublet (1.2 Hz). If the above argument (coupling between Cp and P_{ax} is below the limit of resolution) holds, the Ph_2P group in this case occupies a position *trans* to CH_3 in a tetragonal-pyramidal structure.

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