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A Qualitative Study of the Reactions of 3,5-Dimethylpyrazolyldiphenylphosphine with Tetracarbonyl Complexes of Molybdenum(0) and Tungsten(0)

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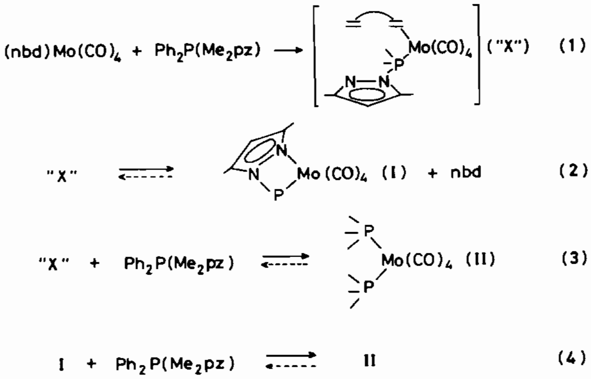
The reactions of diphenyl(3,5-dimethylpyrazolyl)phosphine (LL) with [(nbd)M(CO)$_4$] *(nbd = norbornadiene, M = Mo, W) and with* [(CH$_3$CN)$_2$W(CO)$_4$] *under mild conditions proceed in a stepwise fashion to yield a mixture of products in equilibrium. The four-membered metallocyclic species* (LL)M(CO)$_4$ *and the phosphorus-coordinated complex* cis-[(LL)$_2$M(CO)$_4$] *are formed in competition, being favoured by 1:1 and >2:1 reaction stoichiometries respectively.*

Introduction

We have previously observed that the synthesis of pyrazolylphosphinemolybdenum- and -tungstencarbonyl complexes from [M(CO)$_6$] (M = Mo, W) and their derivatives is complicated by the formation of several phosphorus-containing species in solution [1]. In an attempt to clarify the mechanistic aspects and the equilibria involved in these substitution reactions, and to secure samples of the various intermediates, we have monitored the thermal reactions of Ph$_2$P(Me$_2$pz)(LL)* [2, 3] with [(nbd)M(CO)$_4$]** (M = Mo [4], M = W [5]) and with [(CH$_3$CN)$_2$W(CO)$_4$] [6] in some detail, using i.r., ^{1}H and ^{31}P n.m.r. spectroscopy.

Reactions between LL and [(nbd)(Mo(CO)$_4$] in 1:1 and 2:1 molar ratios in toluene at various temperatures gave ^{31}P signals downfield from LL due to (i) a species 'X', (ii) the previously characterized complex *cis*-[(LL)Mo(CO)$_4$] (I) [1], and (iii) a new complex II, tentatively identified as *cis*-[(LL)$_2$Mo(CO)$_4$] (see below). Thus at room temperature a 1:1 reaction mixture was almost completely converted into species 'X' (δ^{31}P = –90, Δ^{31}P = –51 ppm§), over a period of 6 hours, before small amounts of I and II were observed. The proportion of I increased with time, at the expense of X, until, after 13 days, compound I was the major species present. A 2:1 reaction mixture behaved quite differently. The initial signals indicated II > 'X' ≫ I, followed first by an increase of I at the expense of 'X', then by a slow increase of II at the expense of I. After 26 hours the main species was II.

A study of 2:1 mixtures of LL and [(nbd)Mo(CO)$_4$] at low temperatures (–12°, –23° and –78 °C) showed that I and II were the first dominant products, followed by a slower growth of 'X'. The low temperature reactions were quite slow, as evidenced by the presence of free ligand, 'X', I and II even after one month at –12 °C. It seems likely that 'X' represents the first stage in the displacement of the diolefin from [(nbd)Mo(CO)$_4$], and hence may be represented as [(LL)(nbd)Mo(CO)$_4$], in which LL and nbd are monodentate (equation 1). Subsequent events appear to be a slow cyclization step, giving I (equation 2), and, in the presence of excess LL, a relatively rapid conversion of 'X' into II (equation 3). In addition, there is a relatively slow reaction of I with LL to yield II (equation 4). In all of the above cases, several transient upfield ^{31}P signals of low intensity were observed (Δ^{31}P at +5 to –15 ppm). These signals may correspond to monodentate N-coordinated species, analogous to N-coordinated [PhP(Me$_2$pz)$_2$Mo(CO)$_3$], for which Δ^{31}P is +17 ppm [1].



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*Me$_2$pz = 3,5-dimethylpyrazolyl.

**nbd = norbornadiene.

§Δ^{31}P = coordination chemical shift = (δ^{31}P complex – δ^{31}P ligand.

Compound I was isolated as an analytically pure yellow solid, with spectroscopic properties indentical to those of *cis*-[(LL)Mo(CO)$_4$] [1]. We were unable to obtain pure samples of II, however, partly because of its tendency to equilibrate with I and LL in solution. The lability of II may be attributed to steric destabilization resulting from the *cis* arrangement of the bulky Ph$_2$P(Me$_2$pz) ligands. Similar steric effects are observed for the *o*-tolylphosphines Ph$_x$P(*o*-tol)$_{3-x}$ [7–11]; the 2-methyl group of Ph$_2$P(*o*-tol) and the 5-methyl group of Ph$_2$P(Me$_2$pz) are similarly located with respect to the donor phosphorus centre, resulting in comparable cone angles [12] and steric requirements for these ligands. The i.r. (ν(CO) region, 2024(m), 1921(s), 1898(s), 1865(s) cm^{-1}) and ^{1}H n.m.r. spectra of a slightly impure sample of II were similar to those of *cis*-[(LL)$_2$W(CO)$_4$] (IV) (see below). The ^{31}P chemical shift for II ($\delta\,^{31}$P = –104 ppm)[†] was 26 ppm to lower field than for IV, consistent with the differences reported for [(R$_3$P)$_2$-M(CO)$_4$], [(Ph$_x$Bu$_{3-x}$P)$_2$M(CO)$_4$] and [((MeO)$_3$P)$_3$-M(CO)$_4$] molybdenum and tungsten systems [13, 14]. The mass spectrum of II showed fragments at 596 a.m.u., corresponding to the expulsion of Me$_2$-pz and Ph from the parent ion, and at 540 and 484 a.m.u.'s, indicating the pairwise loss of CO ligands. On the basis of the above data, II and IV appear to be the analogous species *cis*-[(LL)$_2$M(CO)$_4$].

The reaction of LL with [(nbd)W(CO)$_4$] approximately 3:1 molar ratio) in benzene was monitored at 75 °C. The first ^{31}P n.m.r. signal to appear was attributable to the previously characterised *cis*-[(LL)W(CO)$_4$] (II) [1], showing that cyclisation was favoured over *cis* substitution, despite the relatively high proportion of ligand present. The signal due to the new compound *cis*-[(LL)$_2$W(CO)$_4$] (IV) appeared later and developed more slowly. Thus only two phosphorus-coordinated species were detected, contrasting with three in the reactions of [(nbd)Mo-(CO)$_4$]. The absence of a detectable species corresponding to the partial displacement of the diolefin from [(nbd)W(CO)$_4$] may be attributed to the more vigorous thermal conditions employed.

The reaction of LL with [(CH$_3$CN)$_2$W(CO)$_4$] (~3:1 molar ratio) was followed at room temperature. The facile displacement of coordinated acetonitrile has been described [15]. The dominant product throughout the study (44 hours) was IV, together with small amounts of III and a species 'Y'. Thus a preference for *bis*-substitution, rather than cyclisation was indicated. The partially substituted intermediate [(LL)(CH$_3$CN)W(CO)$_4$] ($\delta\,^{31}$P = –76 ppm) is a possible formulation for 'Y'; further reaction with LL, or intramolecular cyclisation, would lead to IV and III, respectively.

The formulation of IV as *cis*-[(LL)$_2$ W(CO)$_4$], in which the LL ligands are monodentate via phosphorus, is based upon analytical, i.r. (ν(CO) region), ^{1}H and ^{31}P n.m.r. data (see Experimental section). The i.r. spectrum showed four ν(CO) bands at energies typical of various *cis*-[(R$_3$P)$_2$M(CO)$_4$] derivatives [16]. The proton decoupled ^{31}P n.m.r. spectrum consisted of a single resonance, with ^{183}W satellites downfield from LL, indicating equivalent phosphorus nuclei directly bound to the metal centre [17–19]. The ^{1}H n.m.r. spectrum of IV showed a phenyl multiplet, a broad singlet due to the 4-H of the Me$_2$pz ring, and two pairs of closely spaced, equal intensity resonances for the methyl protons. The splitting of the methyl resonances is not observed in other less crowded dimethylpyrazolylphosphine complexes [1]. In this instance it suggests that the rotation of the Me$_2$pz ring about the P–N bond is restricted on the n.m.r. time scale, on account of the *cis* arrangement of the bulky Ph$_2$P-(Me$_2$pz) ligands. In the *trans* isomers of [(LL)$_2$-W(CO)$_4$] (M = Mo, W), the steric crowding is relieved and only two methyl ^{1}H resonances are observed [1]. Trends in the chemical shifts and coupling constants for *cis*- and *trans*-[(LL)$_2$W(CO)$_4$] are consistent with reported data on related systems [14].

In the reactions of LL with [(nbd)M(CO)$_4$] and [(CH$_3$CN)$_2$W(CO)$_4$] described above, it is noteworthy that there was no ^{31}P n.m.r. evidence for the formation of the *trans* isomers [(LL)$_2$M(CO)$_4$], even when reaction mixtures were allowed to stand for several weeks. Clearly, the mild reaction conditions favour the *cis* isomers [16, 20–22]. However, a reasonably rapid dissociative loss of LL from *cis*-[(LL)$_2$M(CO)$_4$] is to be expected [16]. The resulting coordinatively unsaturated intermediate must either retain its C$_s$ stereochemistry [23] prior to a reversible uptake of LL, or become coordinatively saturated via intramolecular cyclisation. In both cases *cis–trans* isomerization would be inhibited. Under more vigorous thermal conditions, and in the presence of excess ligand, however, the *trans* isomers are formed [1].

Experimental

All experimental operations were carried out under anhydrous and oxygen-free conditions, using high vacuum or inert atmosphere systems. Solvents were dried by standard methods and distilled under nitrogen before use. The following reagents were prepared according to published procedures: Ph$_2$P(Me$_2$pz)(LL) [2]; [(nbd)Mo(CO)$_4$] [4]; [(nbd)-W(CO)$_4$] [5]; and [(CH$_3$CN)$_2$W(CO)$_4$] [6].

[†] The $\delta\,^{31}$P and Δ^{31}P data reported in error for *trans*-[(LL)$_2$-Mo(CO)$_4$] in reference [1] in fact correspond to the *cis* isomer.

Elemental analyses for C, H and N were performed by the University Analyst, Simon Fraser University. Infrared spectra were recorded with a Perkin-Elmer 457 spectrophotometer, with a solvent compensating cell in the reference beam, and were calibrated against standard polystyrene film. ^1H and ^{31}P n.m.r. spectra were measured using a Varian XL100 instrument operating in the Fourier transform mode, with chemical shifts referred to internal tetramethylsilane and external 85% H_3PO_4, respectively. Mass spectra were determined with a Hewlett Packard 5985 GC/MS instrument, using 70 eV electron impact excitation.

N.m.r. Study of Reactions of $Ph_2P(Me_2pz)$ with $[(nbd)Mo(CO)_4]$

A toluene solution containing equivalent concentrations (~0.4 *M*) of $Ph_2P(Me_2pz)$ and $[(nbd)Mo(CO)_4]$ was allowed to react at room temperature. Toluene solutions containing $Ph_2P(Me_2pz)$ (~0.1 *M*) and $[(nbd)Mo(CO)_4]$ (~0.05 *M*) were allowed to react: (a) at room temperature; (b) at −12 °C, in a refrigerator; (c) at −23 °C, in a CCl_4 slush bath; and (d) at −78 °C, in a dry ice/acetone bath. The probe temperature of the n.m.r. spectrometer was adjusted to correspond with the temperature of the reaction under study. ^{31}P n.m.r. spectra were taken at intervals for periods of 3–8 weeks. Infrared spectra of the reaction mixtures were taken at intervals, and of products obtained on workup (see Discussion).

Preparation of cis-*$[(Ph_2P(Me_2Pz))_2W(CO)_4]$*

A mixture of $Ph_2P(Me_2pz)$ (0.5 g, 1.8 mmol) and $[(CH_3CN)_2W(CO)_4]$ (0.25 g, 0.6 mmol) in benzene (20 ml) was stirred under N_2 for 20 hours. The solvent was removed under vacuum, giving a pale yellow solid which was recrystallised from Et_2O/hexane. Yield, 0.3 g (53%); m.p., 90 °C (dec). *Anal.*, calcd. for $C_{38}H_{34}N_4O_4P_2W$, C 53.26, H 4.00, N. 6.54; found, C 52.9, H 4.04, N 6.67%. I.r. spectrum in chloroform (ν_{CO} region): $A_1^{(2)}$ 2020(m), $A_1^{(1)}$ 1920(s), B_1 1900 (s), B_2 1880(sh). ^1H n.m.r. spectrum, in $CDCl_3$: τ 2.27–2.53 (phenyl multiplet), 3.97 (broad; 4H of Me_2pz ring), 7.70, 7.78, 8.62, 8.68 (3-methyl and 5-methyl protons of the Me_2pz ring). ^{31}P n.m.r. spectrum, taken under broad band proton decoupling conditions, $\delta^{31}P$ (rel. to H_3PO_4) at −78 ppm, $\Delta^{31}P$ = −38 ppm; from the observed ^{183}W side-bands, $J(^{31}P–^{183}W)$ = 276 Hz. The mass spectrum of $[(Ph_2P(Me_2pz))_2W(CO)_4]$ showed fragments at a.m.u. 684 (corresponding to the loss of Ph and Me_2pz from the parent ion), 668 (further loss of CH_4) and at 576, 520 and 464, corresponding to $Ph_2P(Me_2pz)W(CO)_4$, $Ph_2P(Me_2pz)W(CO)_2$ and $Ph_2P(Me_2pz)W$ respectively.

N.m.r. Studies of the Reactions of $Ph_2P(Me_2pz)$ with (a) $[(nbd)W(CO)_4]$ and (b) $[(CH_3CN)_2W(CO)_4]$-$[(CH_3CN)_2W(CO)_4]$

Reaction mixtures containing the ligand and $[(nbd)W(CO)_4]$ or $[(CH_3CN)_2W(CO)_4]$ (in ~3:1 molar ratios) in benzene were monitored by ^{31}P n.m.r. spectroscopy at 75 °C and room temperature, respectively. The time dependent spectra are described in the text.

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