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Reactions of Five-coordinate Molybdenum(0) and Tungsten(0) Complexes $[PhP(Me_2pz)_2M(CO)_3]$ with Small Molecules

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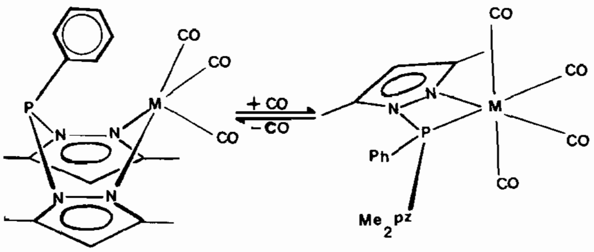
The coordinatively unsaturated species $[PhP(Me_2pz)_2M(CO)_3]$ (Me_2pz = 3,5-dimethylpyrazolyl; M = Mo, I; M = W, II) react reversibly with CO, and irreversibly with H_2, C_2H_4, $P(OMe)_3$ and PF_3, but not with N_2 and Ph_3P. The tricarbonyl/tetracarbonyl interconversion (I, II) + CO $\rightleftarrows$ $[PhP(Me_2pz)_2M(CO)_4]$ (III, M = Mo; IV, M = W) involves a novel structural interchange between the pseudo C_{3v}, phosphorus-free, six-membered [P(N–N)$_2$M] boat metallocyclic form of I and II, and the pseudo C_{2v}, phosphorus-coordinated, four-membered [$\overline{PNNM}$] metallocyclic structures of III and IV. The reaction of I with PF_3 gives $[PhP(Me_2pz)_2Mo(CO)_2(PF_3)_2]$ (V), in which the pyrazolylphosphine ligand again defines a four-membered [$\overline{PNNMo}$] chelate structure. A trans-*dicarbonyl,* cis-(bis-*trifluorophosphine) arrangement is indicated.*

The complexes $[PhP(Me_2pz)_2M(CO)_3]$ (Me_2pz = 3,5-dimethylpyrazolyl; M = Mo, I; M = W, II) [1, 2] have similar i.r., ^1H and ^{31}P n.m.r. spectra, and presumably have similar, coordinatively unsaturated pseudo C_{3v} structures in solution. A crystal structure determination [3] showed that II is mononuclear with a six-membered [P(N–N)$_2$W] boat metallocyclic skeleton, a structure common among complexes of pyrazolylborate [4, 5] and pyrazolylgallate [6, 7] ligands. Five of the approximately octahedral positions about W are occupied by three CO's and two N atoms. The sixth coordination site is sterically blocked by the phenyl ring, which adopts an *endo* orientation in the boat metallocycle. We report here our studies of the reactions of I and II with small molecules.

Compounds I (orange-red) and II (dark red) are slightly soluble in hexane, benzene and toluene, and reasonably soluble in chloroform, dichloromethane, acetonitrile, acetone and tetrahydrofuran. The chloroform solutions of I and II are unstable, slowly becoming brown and developing a number of low-field ^{31}P resonances. All of the above solutions are unstable in air.

The reactions of I and II with small molecular species were studied using i.r., ^1H and ^{31}P n.m.r. spectroscopic methods, in deuterated solvents where required. Dinitrogen, dihydrogen and ethylene did not react with I and II under ambient conditions. This contrasts with the ready, reversible reactions reported for the coordinatively unsaturated species $[M(CO)_3(PCy_3)_2]$ (M = Mo, W; Cy = cyclohexyl) [8]. At 60 °C, however, compound I does react with H_2 and with C_2H_4, producing greenish-black solutions. No ^1H n.m.r. signal due to Mo–H could be detected. With carbon monoxide, a slurry of I or II in various solvents was found to react readily, producing a homogeneous yellow solution of $[PhP(Me_2pz)_2M(CO)_4]$ (M = Mo, III; M = W, IV). On flushing the solution with dinitrogen, the original compounds I and II were quickly regenerated. The $[M(CO)_3(PCy_3)_2]$ complexes, however, coordinate CO irreversibly [8]. The (I, II) + CO $\rightleftarrows$ (III, IV) interconversion can be repeated in a cyclic fashion a number of times, but eventually an irreversible change to a yellow, difficult to separate, multi-component solution occurs. Two of the products were identified as $[Mo(CO)_6]$ and $[Ph(Me_2pz)_2PMo(CO)_5]$, a phosphorus-coordinated analogue of $[(Ph_3P)Mo(CO)_5]$ [9].

From infrared evidence (ν(CO) region), the complexes III and IV [2] have similar *cis*-tetracarbonyl, pseudo C_{2v} structures (ν(CO): complex III (in toluene), 2022(s), 1913(vs), 1976(br,s); complex IV (in $CHCl_3$), 2020(s), 1915(vs), 1895(m), 1860(m)). In both cases ^1H n.m.r. data (in $CDCl_3$ and C_6D_6) indicated non-equivalent Me_2pz rings, and the ^{31}P coordination chemical shifts (in toluene (for III) and $CDCl_3$ (for IV)). (−67 ppm for III, −45 ppm for IV) showed that the phosphorus atom was directly bonded to the metal. The corresponding coordination shifts for I and II were +17 and +19 ppm, respectively [2]. These results signify a dramatic structural change from the [P(N–N)$_2$M] six-membered boat metallocyclic form of I and II, in which the Me_2pz rings are equivalent and the P atom is free, to a structure based upon a four-membered [$\overline{PNNM}$] metallocycle in which only one of the two pyrazolyl rings, and the phosphorus atom, are coordinated to the metal centre. We examined CPK molecular models (CPK Atomic Models, Ealing Scientific Limited, 23 Leman Street, London, E.1., England) of coordinatively saturated, boat metallocyclic forms of six-coordinate III or IV. A severe steric interaction between the *endo*-phenyl group and the additional carbonyl group (the 'sixth' ligand) was noted. A possible rearrangement to an *exo*-phenyl orientation is hindered by steric interactions with the 5-methyl groups of the Me_2pz rings. A model of the proposed four-membered metallocyclic structure of III and IV is relatively uncrowded, suggesting that the structural reorganization is sterically driven:



Interestingly, the complex $[PhP(Me_2pz)_2Re(CO)_3Br]$ maintains a six-membered, $[P(N{-}N)_2Re]$ boat metallocyclic structure, with the phenyl group and Br, rather than CO, in *endo* positions [3].

The attempted synthesis of III via the reaction of $PhP(Me_2pz)_2$ with $[(nbd)Mo(CO)_4]$ (nbd = norbornadiene) was monitored using ^{31}P n.m.r. spectroscopy. Several phosphorus containing products, formed in a stepwise sequence, were observed. The ultimate equilibrium mixture contained I, III and other products, and was difficult to resolve completely into pure, identifiable components. The corresponding reaction with $[(nbd)W(CO)_4]$ yields pure IV [2].

Ligand uptake studies (ambient temperature) with tertiary phosphines showed that Ph_3P does not react with I, whereas $(MeO)_3P$ readily displaced $PhP(Me_2pz)_2$ to yield $[Mo(CO)_3(P(OMe)_3)_3]$ [10]. A toluene slurry of I reacted irreversibly with PF_3, giving a yellow solution of $[PhP(Me_2pz)_2Mo(CO)_2(PF_3)_2]$ (V). The $^{31}P\{^1H\}$ n.m.r. spectrum of V in toluene, consisting of a quartet of multiplets, was indicative of an AX_3BY_3C spin system ($J(^{31}P{-}^{19}F) \cong 1300$ Hz). The spectrum collapsed, under ^{19}F decoupling, to a broad doublet (intensity = 2; $\Delta^{31}P(PF_3) = -12$ ppm; $J(P{-}P) = 42$ Hz) and a broad triplet (intensity = 1; $\Delta^{31}P$(pyrazolylphosphine) = −40.5 ppm; $J(P{-}P) = 42$ Hz). The ^1H n.m.r. spectrum of V, in $CDCl_3$, showed that the Me_2pz rings were non-equivalent, and the i.r. spectrum showed two ν(CO) bands (2035(m), 1959(vs) cm^{-1}, in $CDCl_3$). Thus, the pyrazolylphosphine ligand again defines a four-membered $[\overline{PNNMo}]$ chelate structure. A *trans*-dicarbonyl [10,11] *cis*-bis(trifluorophosphine) geometry seems indicated for the remaining pairs of ligands.

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