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The Nature of Phosphorus(III) Ligands As Probed by Molybdenum-95 NMR Spectroscopy

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The effectiveness of a phosphorus(III) compound (i.e. PY_3, Y = H, R, Ar, OR, NR_2, halide) as a ligand for a transition metal depends upon a combination of its σ-donating, π-accepting, and steric properties. Common measures of the coordinating ability of a phosphorus(III) ligand include its Bronsted basicity (given by pK_a),[1] the coordination chemical shift of the ^{31}P NMR resonance [$\Delta\delta(^{31}P)$, in ppm],[2] the size of the PY_3 ligand (estimated by the cone angle, θ),[3] and the magnitude of the trans-carbonyl infrared stretching frequency in its metal carbonyl complexes [e.g. the electronic parameter χ is derived from the $\nu(CO)$ A_1 mode in $Ni(CO)_3(PY_3)$ compounds].[3a,4,5] Although widely utilized, these parameters have serious limitations. For example, pK_a only measures the ligand σ-donicity, i.e. interaction with the proton. Similarly, $\Delta\delta(^{31}P)$ reflects primarily a property of the free ligand rather than the complex since its magnitude may depend more on C–P–C bond angle changes than the strength of the M–P interaction. Cone angles for PY_3 are estimates of limiting values,[3a] whereas a range of θ and "ligand profiles" are possible.[3b] The differentiation of σ- and π-properties of PY_3 ligands derived from carbonyl infrared data rests upon an *assumption* of their relative influence on cis- and trans-carbonyl bonds.[6] In this communication, we suggest the utility of the ^{95}Mo NMR chemical shift as a very sensitive indicator of the total coordinating ability of phosphorus(III) ligands. To illustrate this application, we present ^{95}Mo NMR spectroscopic evidence to show that, in variance with the widely accepted conclusions based on carbonyl infrared data,[5-7] PCl_3 and related chlorophosphine ligands are very weak π-acceptors and are not strong π-acceptors like PF_3.

In extending our ^{95}Mo NMR studies of $Mo(CO)_{6-n}L_n$ (n = 0–3, L = N, P, As, Sb ligands) complexes[8] to an extensive series of *fac*-$Mo(CO)_3(PY_3)_3$ (Y = R, Ar, OR, NR_2, halide) complexes, we have found that $\delta(^{95}Mo)$ varies from −1860 ppm[9] for the PF_3 case to −910 ppm for the PCl_3 derivative. The large deshielding effect of the PCl_3 ligand was doubly surprising, given the expectation that PCl_3 was virtually equal to PF_3 in π-acceptor ability and that an earlier report[10] gave $\delta(^{95}Mo)$ = −1885 ppm for the *fac*-$Mo(CO)_3(PCl_3)_3$ complex. Our observation of ^{95}Mo chemical shift values for *fac*-$Mo(CO)_3(PPh_{3-n}Cl_n)_3$ (n = 0–2) of −1265, −1319, and −1124 ppm, respectively, verify the authenticity of the extreme downfield position of the resonance for the PCl_3 complex. As previously found for mono- and disubstituted molybdenum carbonyl complexes,[8a,b] the other PY_3 complexes show the shielding order $PR_3 < P(OR)_3 < PF_3$. Discussion of the factors influencing the shielding of the quadrupolar molybdenum nucleus ($I = {}^5/_2$, $Q = -0.015 \times 10^{28}$ m² for ^{95}Mo) requires consideration of the dominant paramagnetic term

$$\delta \propto -\sigma_p = \Delta E^{-1} \langle r^{-3} \rangle_d k^2$$

Although the "nephelauxetic" contribution to σ_p can predominate {e.g. $\delta(^{95}Mo)$ occurs upfield for $[Mo(CO)_5X]^-$ in the order X = Cl < Br < I}[11,12] due to greater d-orbital expansion and bond covalency, the "spectrochemical" ΔE term is known to be most important for a series with similar ligands such as common phosphorus(III) ligands.[8,12,13]

In order to differentiate the relative importance of σ-donor and π-acceptor effects to the magnitude of the HOMO–LUMO ΔE gap for the present series of *fac*-$Mo(CO)_3(PY_3)_3$ complexes, we have plotted in Figure 1 the Kabachnik $\sum\sigma^{ph}$ parameter[14] for some representative PY_3 ligands against the $\delta(^{95}Mo)$ values. The Kabachnik substituent parameters, derived from ionization data of phosphoric acids using a Hammett-type relationship, have been employed by earlier workers[1b,3a] to judge the transmission of electronic effects through phosphorus in PY_3 ligands. We found earlier for a series of $Mo(CO)_3(bipy)P(C_6H_4\text{-}X\text{-}p)_3$ complexes that correlations of $\delta(^{95}Mo)$ with $\sum\sigma^{ph}$ were superior to those against pK_a, $\Delta\delta(^{31}P)$, χ, and $\nu(CO)$.[15] The importance of the π-acceptor ability of PY_3 in causing greater shielding on the molybdenum atom is shown by the high-field resonance for the complexes of PF_3 and the phosphites. Indeed, the near invariance of $\delta(^{95}Mo)$ values in the series $Mo(CO)_{6-n}(PF_3)_n$ (n = 0–6) shows the equivalence of the π-acceptor ability of CO and PF_3, not the insensitivity of $\delta(^{95}Mo)$ to the electronic environment.[16] It should be noted, however, that molybdenum d-orbital expansion via the π-interaction would also contribute to the molybdenum atom being more shielded. Similarly, the deshielded $\delta(^{95}Mo)$ values observed for the PR_3 and PPh_3 complexes can be mainly attributed to the decreased π-acceptor ability of these PY_3 ligands since

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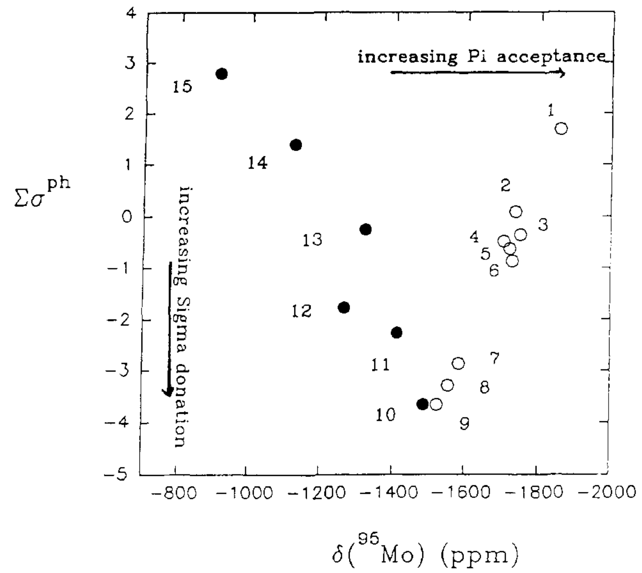

Figure 1. Graph of $\delta(^{95}Mo)$ for [*fac*-$Mo(CO)_3L_3$] against Kabachnik's parameter $\Sigma\sigma^{ph}$ for the substituents of the phosphorus ligands: 1, PF_3; 2, $P(OCH_2CH_2Cl)_3$; 3, $P(OMe)_3$; 4, PH_2Ph; 5, $P(OEt)_3$; 6, $P(OPr^i)_3$; 7, PMe_3; 8, PEt_3; 9, PBu^n_3; 10, $P(NMe_2)_3$; 11, $PEtPh_2$; 12, PPh_3; 13, $PClPh_2$; 14, PCl_2Ph; 15, PCl_3.

their increased σ-basicity relative to PF_3 and their expectedly greater covalent interaction should have increased the subsequent shielding.

In earlier ^{95}Mo NMR studies of $Mo(CO)_{6-n}(PY_3)_n$ ($n = 1, 2$) complexes we gave evidence of steric effects being superimposed on electronic effects.[8a,b] The expectation that $\delta(^{95}Mo)$ will be even more deshielded for bulky PY_3 ligands relative to smaller ones for the present fac series was borne out by the data. For example, $\delta(^{95}Mo)$ values[8a,b,12] for the $Mo(CO)_{6-n}[P(OMe)_3]_n$ ($n = 1$–3) complexes (−1864, −1827, and −1749 ppm, respectively) show a regular deshielding for the relatively small phosphite ($\theta = 107°$).[3a] In contrast, the ^{95}Mo chemical shifts for the $Mo(CO)_{6-n}(PPh_3)_n$ ($n = 1$–3) complexes (−1743, −1556, and −1265 ppm) show an irregular enhanced deshielding with increasing degree of substitution for the larger PPh_3 ($\theta = 145°$). Determination of the "steric threshold" and quantification of the steric effect are being sought in further ^{95}Mo NMR studies.

The dramatic and initially surprising deshielding effect observed for the $PClPh_2$, PCl_2Ph, and PCl_3 complexes can only be explained by their combination of low basicity ($\Sigma\sigma^{ph} = -0.25$, 1.38, and 2.79 and $\chi = 23.4$, 33.9, and 44.4, respectively) and very low π-acceptor ability. In contrast, *fac*-$Mo(CO)_3(P(OMe)_3)_3$ has $\delta(^{95}Mo)$ at −1749 ppm even though the basicity of $P(OMe)_3$ is similar ($\Sigma\sigma^{ph} = -0.36$, $\chi = 23.1$) to that of $PClPh_2$; so the great decrease in molybdenum shielding for the latter case [$\delta(^{95}Mo) = -1319$ ppm] must be due to much reduced π-acceptor ability. Several other $Mo(CO)_3L_3$ complexes with nitrogen and oxygen ligands of no feasible π-acceptor ability show $\delta(^{95}Mo)$ resonances downfield of −1000 ppm.[17] Given that PF_3 has a basicity [$\Sigma\sigma^{ph} = 1.68$] that is intermediate to those of PCl_2Ph and PCl_3, the large difference in $\delta(^{95}Mo)$ values must be attributed to the much decreased π-acceptor nature of the chlorophosphines. Their low σ-donor ability is compatible with immeasurably low pK_a values and large, positive Kabachnik values, but our results reverse the commonly accepted order of π-acceptor properties, given as $PPh_3 < PClPh_2 < PCl_2Ph < PCl_3$.[5-7] Our conclusions from ^{95}Mo NMR spectroscopy that chlorophosphines have very weak σ-donor and π-acceptor properties is supported by earlier reports of the low bond strength[18] and the facile ease of exchange[19] of the Mo–PCl_3 bond. The earlier report[10] that $^1J(Mo–P) = 251$ Hz for *fac*-$Mo(CO)_3(PCl_3)_3$, confirmed in this work, is still entirely consistent with PCl_3 having low π-acceptor ability. In our view, the magnitude of the coupling constant simply reflects the s-character of the Mo–P bond, not the σ-bond strength nor its enhancement by synergistic π-bonding, and is primarily a function of the electronegativity of the substituent. Similarly, the enhanced magnitude of 2041 cm^{-1} for $\nu(CO)(A_1)$ of the PCl_3 complex, compared to 1948 cm^{-1} for the PPh_3 case (and 2065 cm^{-1} for the PF_3 complex), is actually expected[20] as a consequence of the weak σ-donor ability of PCl_3, which weakens the Mo–C dπ–pπ bond. The common assumption that the A_1 mode of infrared carbonyl stretching frequencies reflects primarily the π-acceptor ability of a trans PY_3 ligand[5-7] should not be invoked for PCl_3 and the other chlorophosphine ligands or for any weak σ-donor ligand with weak π-acceptor ability.

In conclusion, we suggest that $\delta(^{95}Mo)$ is a sensitive probe of the nature of phosphorus(III) ligands, with a plot of the Kabachnik electronic parameter $\Sigma\sigma^{ph}$ against $\delta(^{95}Mo)$ allowing a qualitative differentiation of σ- and π-bonding effects. The application to chlorophosphine ligands reverses the widely accepted order of their π-acceptor ability and assigns very low π-acceptor character to PCl_3 as compared to PF_3. Continuing studies involve correlations of $\delta(^{95}Mo)$ with a wider range of PY_3 properties and $Mo(CO)_3(PY_3)_3$ complexes.

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