Inorganica Chimica Acta

LETTER

Steric Effects of Tertiary Phosphines on ^{199}Hg Chemical Shifts in $[\{(\eta^5\text{-}C_5H_5)(CO)_2(L)Mo\}_2Hg]$ Complexes

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(Received February 5, 1990)

A trend to increased shielding of the ^{119}Sn chemical shift in a series of complexes, $[(\eta^5\text{-}C_5H_5)(CO)(L)FeSnMe_3]$, with increase in the Tolman cone angle, θ [1] of L (L = CO, $P(OMe)_3$, $PMePh_2$, PPh_3, $P(CH_2Ph)_3$) has recently been observed [2]. This apparent correlation between a steric effect and an electronic property was interpreted in terms of reduced $(d{-}d)\pi$ bonding between the iron and tin atoms, as the cone angle is increased, arising from the distortion of ligands from the axis of a regular octahedron. The reduction in π bonding was thought to reflect into a reduction in ΔE in the paramagnetic shielding term, σ^p. We now report a similar steric dependence on ^{199}Hg chemical shift in a series of compounds with mercury–molybdenum bonds, $[\{(\eta^5\text{-}C_5H_5)(CO)_2(L)Mo\}_2Hg]$, for L = CO, PMe_2Ph, PEt_3, $PMePh_2$, $PEtPh_2$, $P(i\text{-}Bu)_3$, PPh_3 and PCy_3.

Experimental

The $[\{(\eta^5\text{-}C_5H_5)(CO)_2(L)Mo\}_2Hg]$ complexes were prepared by direct reaction between $[\{(\eta^5\text{-}C_5H_5)(CO)_3Mo\}_2Hg]$ and the appropriate phosphine in refluxing ethanol [3] or, less satisfactorily, in refluxing heptane [4]. The compounds for L = PEt_3, $PEtPh_2$, $P(i\text{-}Bu)_3$ and PCy_3 are previously unreported.

^{199}Hg (at 17.80 MHz) and ^{31}P (at 40.26 MHz) NMR spectra were recorded, in saturated $CDCl_3$ solution, on a Jeol FX100 spectrometer. Chemical shifts are referenced to neat Me_2Hg (coaxial capillary) and to 85% H_3PO_4 (coaxial capillary). ^{1}H NMR spectra were measured on a Jeol PS100 spectrometer in $CDCl_3$ solution relative to internal TMS.

Results and Discussion

The $[\{(\eta^5\text{-}C_5H_5)(CO)_2(L)Mo\}_2Hg]$ compounds, on the basis of ^{1}H NMR studies for L = PMe_2Ph and a crystallographic study of a related complex, *trans*-$[\{(\eta^5\text{-}C_5H_5)(CO)_2(AsMe_2Ph)Mo\}Hg(CN)]$, prepared from $[\{(\eta^5\text{-}C_5H_5)(CO)_2(AsMe_2Ph)Mo\}_2Hg]$ [4], have structures based on a linear geometry around Hg and a *trans*-substituted pseudo square pyramidal geometry around Mo. The *trans* geometry is further supported, on the grounds of Manning's criterion [5], by the observation of small splittings in the ^{1}H cyclopentadienyl resonance ($\delta \simeq 5.0$ ppm, $J(^{31}P{-}^1H) \sim 1$ Hz for L = PMe_2Ph, $PMePh_2$ and PEt_3). The ^{199}Hg spectra show the expected triplet with coupling to two chemically equivalent phosphorus atoms, and the ^{31}P spectra a satellite doublet arising from mercury coupling.

The ^{199}Hg chemical shifts (Table 1 and Fig. 1) for the $[\{(\eta^5\text{-}C_5H_5)(CO)_2(L)Mo\}_2Hg]$ complexes move upfield with increase in the cone angle of the tertiary phosphine. The value for L = CO (cone angle = 95°) does not fit the trend and the apparent ^{119}Sn chemical shift correlation with cone angle, observed previously with this ligand in the $[(\eta^5\text{-}C_5H_5)(CO)(L)FeSnMe_3]$ series [2], is probably fortuitous. Although the ^{199}Hg chemical shifts do not show any

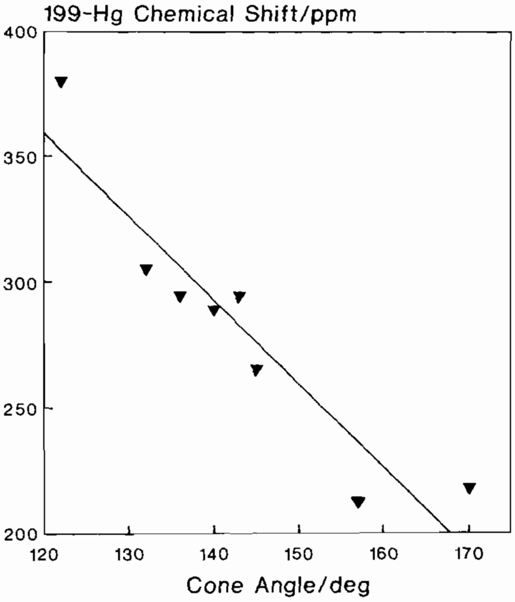

Fig. 1. Plot of variation in ^{199}Hg chemical shift with cone angle of tertiary phosphine for $[\{(\eta^5\text{-}C_5H_5)(CO)_2(L)Mo\}_2Hg]$ complexes.

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0020-1693/90/$3.50

TABLE 1. Spectral data for $[\{(\eta^5\text{-}C_5H_5)(CO)_2(L)Mo\}_2Hg]$ complexes

L	θ	ν	$\delta(^{199}Hg)$	$^2J(^{31}P\text{–}^{199}Hg)$	$\delta(^{31}P)$	$\nu(CO)$		
	(°)	(cm^{-1})	(ppm)	(Hz)	(ppm)	(cm^{-1})		
CO	95		235.3			1998	1969	1888
PPh_3	145	2068.9	265.4	208	57.5	1894	1868	1818
$PMePh_2$	136	2067.0	294.4	215	53.5	1890	1859	1809
$PEtPh_2$	140	2066.7	289.0	212	64.3	1888	1858	1808
PMe_2Ph	122	2065.3	379.9	220	35.2	1886	1855	1804
$P\text{-}t\text{-}BuPh_2$	157	2064.7	212.6	199	78.5			
PEt_3	132	2061.7	305.1	210	50.6	1883	1853	1803
$P(i\text{-}Bu)_3$	143	2059.7	294.4	210	49.1			
PCy_3	170	2056.4	217.8	200	67.3	1877	1849	1798

regular variation with the Tolman electronic parameter, ν [1] of the phosphine, we note that the presence of a significant electronic influence is suggested by observations of the ^{199}Hg chemical shift, in a related system $[\{P(C_6H_4X)_3\}_2(CO)(SnCl_3)(HgCl)ClIr]$ [6], which moves to higher field as the electron-donating capacity of the substituent, in a series of substituted triphenylphosphines of essentially constant cone angle, increases ($\delta = -2077$ ppm for X = p-OCH_3, -2026 ppm for H, and -2002 ppm for p-F). We do not believe that there is a simple explanation for our observed trend but note, on the basis of a previous theoretical analysis [7], that p-orbital effects on the Hg (and Sn) atoms may be somewhat stronger contributors to the σ^P term than those of d-orbitals.

The values of $^2J(^{31}P\text{–}^{199}Hg)$ and the ^{31}P chemical shift exhibit no trend with either the steric or the electronic property of the phosphine. The absorptions in the carbonyl region of the infrared spectra, in $CHCl_3$ solution, show a small, but systematic, movement to lower wavenumber as the electronic parameter of the phosphine decreases (greater basicity).

The complex, $[\{(\eta^5\text{-}C_5H_5)(CO)_2(P(i\text{-}Bu)_3Mo\}_2Hg]$, could not be obtained pure. In addition to the expected resonances, the ^{199}Hg spectrum showed a doublet ($\delta = 298.8$ ppm, $^2J(^{31}P\text{–}^{199}Hg) = 266$ Hz) and the ^{31}P spectrum a satellite doublet ($\delta = 82.8$ ppm). The impurity is tentatively formulated as a singly-substituted species, $[\{(\eta^5\text{-}C_5H_5)(CO)_2(P(i\text{-}Bu)_3)Mo\}Hg\{Mo(\eta^5\text{-}C_5H_5)(CO)_3\}]$.

Acknowledgement

We thank the Australian Research Grants Scheme for financial support.

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