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Preliminary communication

^{31}P NMR COORDINATION SHIFTS OF SOME GROUP VII BIS-PHOSPHINE AND PHOSPHINE—ARSINE CARBONYL COMPLEXES

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Summary

Trends in ^{31}P NMR coordination shifts for the complexes $M(CO)_3BrL_2$, $[M(CO)_3L_2(NCMe)]^+$, $MeC_5H_4Mn(CO)L_2$ and $[MeC_5H_4Mn(CO)_2]_2L_2$ (M = Mn and Re; L_2 = $Ph_2PCH_2PPh_2$, $Ph_2PCH_2CH_2PPh_2$ and $Ph_2PCH_2CH_2AsPh_2$) are discussed.

Introduction

Large ^{31}P NMR downfield chelate coordination shifts were first observed [1] for the complexes $Ni(CO)_2(R_2PCH_2CH_2PR_2)$, (R = Et and CH_2CH_2CN). Later studies using $R_2P(CH_2)_xPR_2$ and $R_2P(CH_2)_xP(O)R_2$, R = alkyl or Ph; x = 1, 2 or 3), substituted carbonyls of chromium, molybdenum, and tungsten [2-6] showed that the ^{31}P chemical shifts of those chelate complexes containing five-membered rings occurred at unusually low fields when compared with analogous $M(CO)_{6-x}(PR_3)_x$ complexes. The extra coordination shift of ca. 30 ppm associated with this chelate effect has been ascribed to ring strain [2] but this is unacceptable because the coordination shifts for $M(CO)_4(Ph_2PCH_2PPh_2)$ complexes possessing more highly strained four-membered rings are substantially less than those of related $M(CO)_4(PR_3)_2$ complexes, (M = Cr, Mo, and W) [4]. It was also observed that when the bis-phosphine ligands coordinated in a bridging rather than in a chelating mode the coordination shifts were not anomalous, being very similar to those found for $M(CO)_{6-x}(PR_3)_x$ complexes.

Results and discussion

During a study of Group VII metal carbonyl—phosphine complexes we have prepared a number of related compounds, (several not previously

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reported), which allow the ^{31}P NMR coordination shifts of bridging and chelating $Ph_2PCH_2PPh_2$ and $Ph_2PCH_2CH_2PPh_2$ to be compared. The chemical shifts ($\delta(P)$) and coordination shifts ($\Delta(P)$) are listed in Table 1. Although several solvents and solutions of various concentrations were employed in obtaining the spectra, concentration and solvent effects were less than 1 ppm and do not affect conclusions drawn from this work.

The results for the chelate complexes I-VIII show that $\Delta(P)$ decreases in the order Mn > Re,(Δ(P)Mn-dppm — Δ(P)Re-dppm) being ca. 49 ppm and (Δ(P)Mn-dppe — Δ(P)Re-dppe) being ca. 36 ppm for pairs of analogous compounds. $\Delta(P)$ decreases in the similar order Cr > Mo > W, for Group VI $M(CO)_4(Ph_2P(CH_2)_xPPh_2)$ ($x = 1, 2$, or 3) chelate complexes [4].

From a comparison of the chelate complex pairs I and III, II and IV, V and VII, VI and VIII, and XI and XIII it is seen that $\Delta(P)$ is consistently greater for chelated dppe than for chelated dppm, by amounts ranging from 47.2 to 63.5 ppm. The data for compounds VIII and IX show that $\Delta(P)$ for a dppe chelate complex is greater than that for an analogous monodentate tertiary phosphine complex.

A comparison of $\Delta(P)$ values for the pairs X and XI and VI and IX shows that $\Delta(P)$ values for the four-membered dppm chelate complexes are anomalously small, being substantially less than for monodentate tertiary phosphine complexes. Indeed, for the rhenium complexes II and VI, $\delta(P)$ is surprisingly upfield of $\delta(P)$ of uncomplexed dppm, leading to positive $\Delta(P)$ values.

The $\delta(P)$ and $\Delta(P)$ values for the methylcyclopentadienylmanganese compounds are consistently greater than those of the cationic or carbonyl bromide complexes, although here too $\Delta(P)$ for the chelate complex XI is anomalously small. By comparing the results for XIII and XIV, $\Delta(P)$ is found

TABLE 1

^{31}P NMR DATA FOR LIGANDS AND COMPLEXES [a]

Compound [b]		P ligand [c]	$\delta(P)$ (ppm) [d]	$\Delta(P)$ (ppm) [e]	Solvent
dppm			22.7		$CHCl_3$
dppe			13.2		$CHCl_3$
arphos			12.0		$CHCl_3$
PPh_3			5.3		$CHCl_3$
$Mn(CO)_3Br(dppm)$	(I)	C	− 10.9	− 33.6	CH_2Cl_2
$Re(CO)_3Br(dppm)$	(II)	C	+ 38.5	+ 15.8	$CHCl_3$
$Mn(CO)_3Br(dppe)$	(III)	C	− 67.6	− 80.8	CH_2Cl_2
$Re(CO)_3Br(dppe)$	(IV)	C	− 30.0	− 43.2	$CHCl_3$
$[Mn(CO)_3(dppm)(NCMe)]ClO_4$	(V)	C	− 13.7	− 36.4	$CHCl_3$
$[Re(CO)_3(dppm)(NCMe)]ClO_4$	(VI)	C	+ 35.0	+ 12.3	CH_2Cl_2
$[Mn(CO)_3(dppe)(NCMe)]ClO_4$	(VII)	C	− 73.5	− 86.7	CH_2Cl_2
$[Re(CO)_3(dppe)(NCMe)]ClO_4$	(VIII)	C	− 38.0	− 51.2	$(CH_3)_2CO$
$[Re(CO)_3(PPh_3)_2(NCMe)]ClO_4$	(IX)	M	− 8.9	− 14.2	$(CH_3)_2SO$
$MeC_5H_4Mn(CO)_2(PPh_3)$	(X)	M	− 96.0	−101.3	$CHCl_3$
$MeC_5H_4Mn(CO)(dppm)$	(XI)	C	− 58.4	− 81.1	C_6H_6
$[MeC_5H_4Mn(CO)_2]_2(dppm)$	(XII)	B	− 91.0	−113.7	$CHCl_3$
$MeC_5H_4Mn(CO)(dppe)$	(XIII)	C	−122.0	−135.2	$CHCl_3$
$[MeC_5H_4Mn(CO)_2]_2(dppe)$	(XIV)	B	− 91.0	−104.2	$CHCl_3$
$MeC_5H_4Mn(CO)(arphos)$	(XV)	C	−122.0	−134.0	C_6H_6
$[MeC_5H_4Mn(CO)_2]_2(arphos)$	(XVI)	B	− 87.0	− 99.0	$CHCl_3$

[a] Spectra obtained using a JEOL-PS-100 spectrometer with an operating frequency of 40 MHz. [b] dppm = $Ph_2PCH_2PPh_2$; dppe = $Ph_2PCH_2CH_2PPh_2$; arphos = $Ph_2PCH_2CH_2AsPh_2$. [c] C = chelating; M = monodentate; B = bridging. [d] Relative to 85% phosphoric acid (coaxial internal capillary). [e] $\Delta(P)$, coordination shift, = δ(complex) — δ(ligand).

to be much greater for chelating dppe than for bridging dppe, Δ(P) for XIV being very similar to that of the monodentate phosphine complex X. On the other hand the results for XI and XII show that Δ(P) for a bridging dppm complex is greater than that of a chelating dppm complex, due to the exceptionally low Δ(P) values of dppm chelates.

Finally, the results for XV and XVI indicate that the large downfield coordination shift established for dppe chelates is also observed when the phosphine—arsine $Ph_2PCH_2CH_2AsPh_2$ coordinates in the same manner. Δ(P) is ca. 35 ppm less when this ligand adopts a bridging coordination. In fact the Δ(P) values of the dppe chelate XIII and arphos chelate XV are strikingly similar.

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