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CHEMISTRY OF METHINYLTRICOBALT ENNEACARBONYLS

X*. ISOMERISM AND NON-RIGID BEHAVIOUR OF PHOSPHINE DERIVATIVES

T.W. MATHESON and B.H. ROBINSON

Department of Chemistry, University of Otago, Dunedin (New Zealand)

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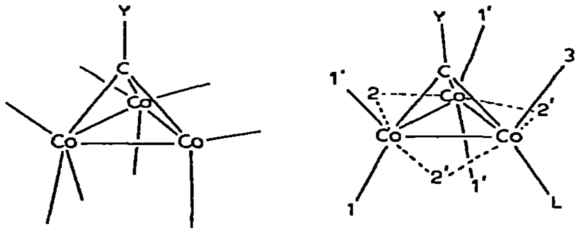
Summary

Variable-temperature infrared and NMR spectra of some phosphine-substituted methinyltricobalt enneacarbonyls are described and interpreted in terms of isomer distribution and intramolecular carbonyl scrambling.

A number of phosphine and arsine derivatives of the tricobalt carbon cluster have been characterised [2]. Two structural types, distinguished by the presence or absence of bridging carbonyl groups (Fig. 1), were recognised in the crystalline $YCCo_3(CO)_8L$ derivatives [3, 4]. Because eleven or more ν(CO) bands were often observed in their solution infrared spectra it was suggested that both structural forms could exist in equilibrium in non-polar solvents and in one compound, $MeCCo_3(CO)_8PBu_3$, coexist in the crystal [2]. This con-



non-bridged

bridged

Fig. 1. Possible structures for $YCCo_3(CO)_8L$ derivatives.

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[*] For part IX see ref. 1.

clusion has been substantiated by IR studies on $CH_3CCo_3(CO)_8P(C_6H_{11})_3$ and $CH_3CCo_3(CO)_8PBu_3$ described herein. Because interconversion between the non-bridged and bridged forms could involve scrambling of the carbonyl groups and phosphine ligand or the carbonyl groups alone, their non-rigid behaviour in solution was studied by ^{13}C and ^{31}P NMR spectroscopy.

Experimental

The phosphine derivatives were prepared by published procedures [2]. Infrared spectra were recorded on a Perkin—Elmer 225 infrared spectrophotometer using a standard Beckman low-temperature infrared cell with a 4 mm spacer. A series of spectra were run using solutions of known concentrations and in different solvents. By making the reasonable assumption that the extinction coefficient of the totally symmetric A_1 $\nu(CO)$ mode at 2074 cm^{-1} in the non-bridged phenyl derivatives, $PhCCo_3(CO)_8L$, was identical to that of the equivalent mode in the methyl derivative, $CH_3CCo_3(CO)_8L$, it was possible to calculate the concentration of the non-bridged isomer. For example, the extinction coefficient for $PhCCo_3(CO)_8P(C_6H_{11})_3$ is 8694 mol^{-1} cm^{-1} at 295 K in heptane. The optical density for the same band of a 1.55×10^{-3} *M* hexane solution of $CH_3CCo_3(CO)_8P(C_6H_{11})_3$ is 0.2529; hence the concentration of non-bridged isomer is 0.73×10^{-3} *M* or 47% of the total concentration. Activation parameters were calculated by the method described by Noack [5]. Proton magnetic resonance spectra were recorded on a Varian HA-100 and the ^{13}C and ^{31}P spectra using pulse Fourier techniques and broad band-proton noise decoupling. ^{13}C data were obtained on solutions of ^{13}CO enriched samples (50-70%) containing $Cr(acac)_3$ as a relaxation agent. Carbon chemical shifts were measured relative to internal CH_2Cl_2 but are quoted relative to TMS [6]; similarly, phosphorus chemical shifts were measured relative to external P_4O_6 but are quoted relative to 85% phosphoric acid [7].

Results

Bridged—non-bridged interconversion

It was shown earlier that the solution infrared spectrum of the phosphine and arsine derivatives were superimposed spectra of the non-bridged (equatorial ligand) and carbonyl-bridged (axial ligand) isomers, with no evidence, except for $PhCCo_3(CO)_8P(C_6H_{11})_3$, of other structural forms arising from juxtaposition of the phosphine or arsine ligand [2]. It is only the alkyl $CCo_3(CO)_8L$ derivatives which have a carbonyl-bridged configuration in the crystal and an appreciable concentration of bridged isomer in solution at ambient temperatures. Unfortunately, the separation between the A_1 (bridged) and A_1 (non-bridged) modes is often smaller than their band widths so that an accurate determination of the relative concentrations is not feasible. This study is concerned with $CH_3CCo_3(CO)_8P(C_6H_{11})_3$, where the separation is 6 cm^{-1}, and $CH_3CCo_3(CO)_8PBu_3$, for which there is evidence of both bridged and non-bridged isomers in the crystal.

Spectral changes between 346 K and 203 K are typified by those shown in Fig. 2 for $CH_3CCo_3(CO)_8P(C_6H_{11})_3$; the equilibrium shifts towards the bridged

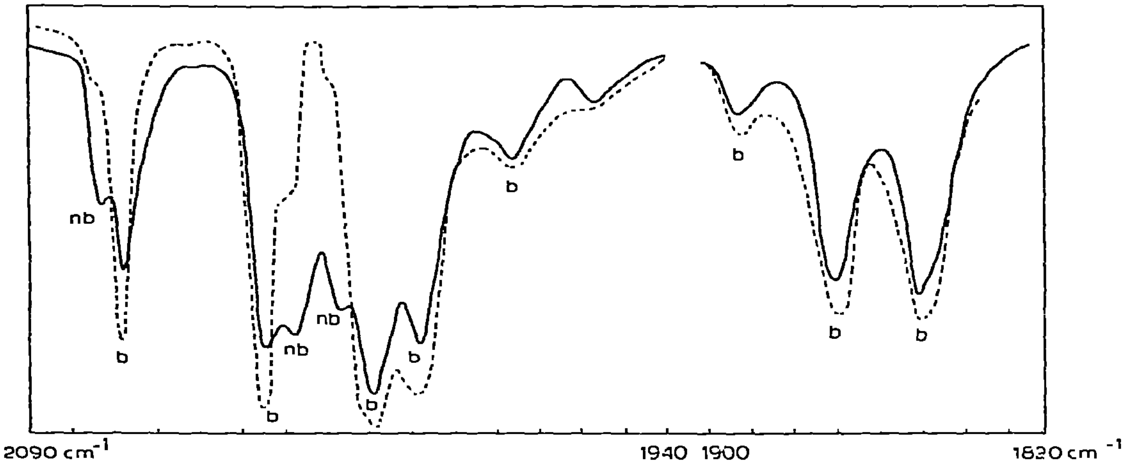

Fig. 2. Variable temperature spectra of $CH_3CCo_3(CO)_8P(C_6H_{11})_3$; — 298 K; - - - 195 K; nb = non-bridged species; b = bridged species.

isomer as the temperature is lowered. Relative isomer percentages and thermodynamic parameters are given in Tables 1 and 2.

Unlike the dimeric cobalt—phosphine complexes $[Co(CO)_3L]_2$ investigated in detail by Manning [8], the relative concentration of the two isomers is largely unaffected by the polarity of the solvent (Table 2), possibly because there is little chance for solvent interaction in these congested molecules. The thermodynamic parameters are consistent with the bridged configuration being the ground-state structure for $CH_3CCo_3(CO)_8P(C_6H_{11})_3$. However, the energy difference between the $CH_3CCo_3(CO)_8PBu_3$ isomers is extremely small and since the overall molecular volume and hence packing requirements of the two isomers are virtually equal it is not surprising that they coexist in the crystal. The formation of a bridged configuration has been attributed to an attempt by the Co_3C moiety to relieve the excess charge on the cluster and it is only with the most basic phosphine ligands that this configuration is stabilised [2]. Analogous phosphite derivatives adopt a wholly non-bridged configuration in solution and the solid [9], phosphites being stronger π-acceptors than phosphines.

TABLE 1

ISOMER DISTRIBUTION (%) IN $CH_3CCo_3(CO)_8L$ [L = $(C_6H_{11})_3P$ AND Bu_3P] COMPLEXES

	Temperature (K)				ΔH	ΔS
	295	273	233	195	(kJ mol^{-1})	(J mol^{-1}K^{-1})
L = $(C_6H_{11})_3P$						
Bridged	64	43	52	88	— 8.6(± 1.5)	23
Non-bridged	66	57	48	12		
L = Bu_3P						
Bridged	34	43	45	52	— 2.0(± 1.7)	9
Non-bridged	66	57	55	48		

TABLE 2

SOLVENT DEPENDENCE OF ISOMER DISTRIBUTION IN $CH_3CCo_3(CO)_8P(C_6H_{11})_3$

Solvent	Total concentration (mol dm^{-3} × 10^{-3})	Non-bridged concentration (mol dm^{-3} × 10^{-3})	% non-bridged
CCl_4	3.67	1.37	37
Heptane	3.11	1.19	38
CS_2	3.95	1.75	41
CCl_4	1.84	0.86	47
Heptane	1.55	0.73	47
CS_2	1.98	1.01	51
CCl_4	0.92	0.47	51
Heptane	0.78	0.39	50
CS_2	0.99	0.49	49

Non-rigid behaviour

The variable temperature ^{13}C and ^{31}P spectra of $CH_3CCo_3(CO)_8P(C_6H_{11})_3$, $CH_3CCo_3(CO)_8PPh_3$ (non-bridged in the crystal), $CH_3CCo_3(CO)_8PBu_3$ and $HCCo_3(CO)_8PMePh_2$ (non-bridged) are shown in Fig. 3. The ^{13}C spectra demonstrate that there is a facile CO-scrambling process which leads to an equivalence of all carbonyl groups at ambient temperatures. Unfortunately, only in the

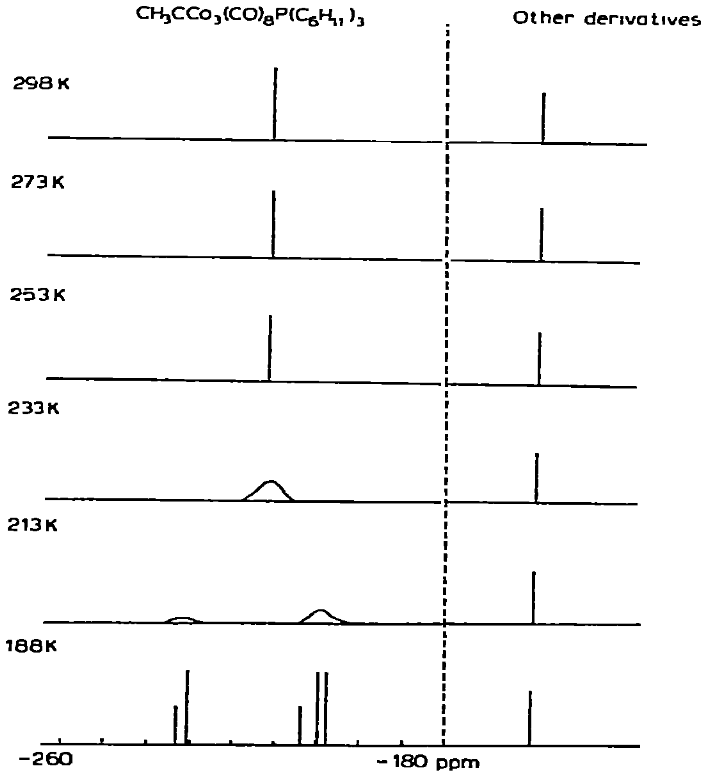

Fig. 3. ^{13}C NMR spectra of phosphine derivatives (schematic).

TABLE 3

^{13}C AND ^{31}P NMR SPECTRA [a]

	Temp. (K)	δ (^{13}C)	Temp. (K)	δ (^{31}P)
$HCCo_3(CO)_8PMePh_2$ [b]	273	−206		
$CH_3CCo_3(CO)_8PPh_3$ [b]	313	−203.9	313	−47.2
	233	−204.5	248	−46.4
	193	−206.7	198	−45.8
$CH_3CCo_3(CO)_8PBu_3$	303	−209.2	303	−29.0
	213	−211.0	193	−21.6
	193	−211.0		
$CH_3CCo_3(CO)_8P(C_6H_{11})_3$	298	−210.9	343	−42.8
	273	−211.0	313	−42.9
	253	−211.7	248	−37.9
	188	−232.9 (1)	188	−35.6
		−230.6 (2)		
		−204.3 (1)		
		−200.0 (2)		
		−198.3 (2)		

[a] Recorded in CH_2Cl_2; values in ppm; ^{13}C chemical shifts with respect to TMS, ^{31}P with respect to H_3PO_4.
[b] J(CP) = 11 Hz.

case of the tricyclohexylphosphine derivative was it possible to obtain the "instantaneous" solution structure, the "frozen" spectrum being compatible with the solid-state CO-bridged configuration [4]. Resonances to lower field at −232.9 and −230.6 ppm can be assigned to the bridged groups, 2 and 2′ respectively (see Fig. 1) the latter resonance being split by ^{31}P coupling [^2J(CP) = 11 Hz]; those at −204.3, −200.0 and −198.3 ppm (relative intensities, 1/2/2 respectively) can be assigned to the terminal carbonyl groups, 3,1′ and 1 respectively. Coalescence occurs at −45°; the appropriate activation parameter is ΔG = − 41.2 kJ mol^{-1}.

Each population-weighted average ^{13}C signal of the other three complexes broadens but does not resolve down to −85°. However the position of this average signal confirms the proposed ground-state structures in solution; the bridged species [$L = P(C_6H_{11})_3$] has a signal downfield (−211 ppm), from the non-bridged [$HCCo_3(CO)_8PMePh_2$, −206.0 ppm: $CH_3CCo_3(CO)_8PPh_3$, −203.9 ppm]. The weighted average signal at −209.2 ppm for the $CH_3CCo_3(CO)_8PBu_3$ complex is consistent with a rapid equilibrating mixture of the two isomers and as expected from the infrared results this average shifts downfield to −211.0 ppm at low temperatures, i.e. it is weighted to the bridged species. It is known that the ^{13}CO resonance is more deshielded the greater the basicity of the phosphine [10] and this is reflected in the ^{13}C resonances of the two non-bridged species.

With all complexes there is a marked downfield shift as the temperature is lowered in both the ^{13}C and ^{31}P resonances. Since this cannot be due to increased concentrations of bridged species, say for the $CH_3CCo_3(CO)_8PPh_3$ complex, it is reasonable to attribute this trend to an increased lifetime of a phosphine ligand on a particular cobalt atom at low temperatures. Extensive phosphine dissociation at room temperature is strongly suggested by the molecular weight data [2].

Conclusion

Before considering a mechanism for the rapid carbonyl scrambling and isomerisation it is necessary to consider in detail the structural differences between the non-bridged and bridged-carbonyl configurations. Besides the obvious equatorial—axial ligand interchange and disparity in coordination number of the cobalt atoms, the formation of three carbonyl bridges causes the angle between the equatorial carbonyl group and the Co_3 plane to increase from 30 to 51°. Moreover, the Co_3 plane is distorted in the bridged configuration (the Co—Co bond opposite the ligand is ≈0.14 Å shorter than the other two) and in the non-bridged configuration the apical group is bent some 10° from the vertical plane bisecting the Co—Co bond and including the third cobalt atom.

A non-bridged—bridged rearrangement therefore involves considerable stereochemical distortion to other parts of the molecule, and it is difficult to see how this rearrangement provides a low-energy path for carbonyl scrambling. In fact, a detailed analysis of this rearrangement shows that it does not lead to complete scrambling and two intramolecular scrambling processes are believed to operate. An intermolecular process is ruled out by the observation of ^{13}CO—phosphorus coupling at ambient temperatures.

Mechanism A

Conrotatory movement of ≈100° about individual cobalt atoms around the basal triangle converts the non-bridged into the bridged configuration (Fig. 4). It is pertinent to note at this point that the angle between the equatorial carbonyls on one cobalt in the non-bridged structure (97°) is virtually identical to the angle between the two terminal carbonyls on one cobalt in the bridged. A sequence of non-bridged—bridged interchanges then leads to scrambling of the *axial* carbonyl groups but not the equatorial. This type of symmetrical three-carbonyl unbridged—bridged permutation has been advanced as a mechanism for carbonyl scrambling in $Rh_4(CO)_{12}$ [11, 12] and similar tetrahedral clusters [13]. The reason for site selectivity in the $YCCo_3(CO)_8L$ case is that a $YCCo_3$ intermediate of T_d symmetry is not accessible and because a phosphine cannot form a bridge. In order to get complete scrambling a pair-wise bridge formation could be advanced but there is no chemical or physical evidence to support this proposal and it can be ruled out on steric grounds alone.

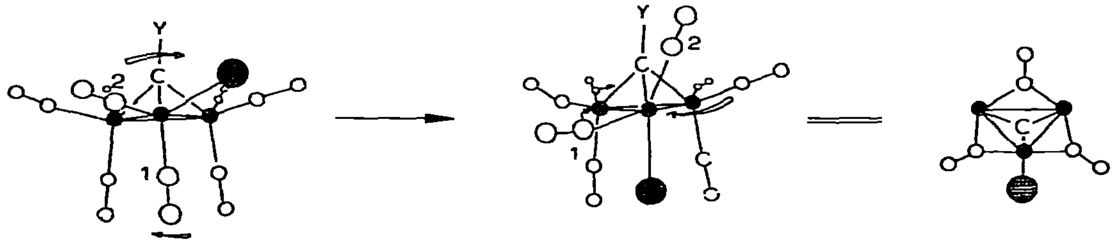

Fig. 4. Mechanism A: non-bridged—bridged interconversion.

Mechanism B

Axial—equatorial interconversion via a twist mechanism about an individual metal which does not involve a net carbonyl transfer from one metal atom to another. All that is required is bending of the CO—M—CO angle to 120° followed by rotation of the $M(CO)_3$ unit by 120°. This is not a remarkable postulate as local scrambling about an individual metal atom is believed to take place in such clusters as $Os_3(CO)_{12}$ and $Ru_3(CO)_{10}(NO)_2$ [14].

A combination of both mechanisms leads to complete carbonyl scrambling and/or conversion from a non-bridged to bridged carbonyl configuration. Bulky phosphines should hinder both mechanistic processes and the slower scrambling in the tricyclohexylphosphine complex is understandable. The parent tricobalt carbon clusters, $YCCo_3(CO)_9$, also show complete carbonyl scrambling down to −100°, presumably via similar mechanisms [9].

Acknowledgement

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