Reactions of $Co_2(CO)_8$ with potentially polydentate phosphines

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Abstract

$Co_2(CO)_8$ reacts with potentially polydentate phosphines such as Ph_2Ppy (2-(diphenylphosphino)pyridine), t-dppv (*trans*-1,2-vinylenebis(diphenylphosphine)), dppa (bis(diphenylphosphino)amine) and dpmp (bis((diphenylphosphino)methyl)phenylphosphine) to give $Co_2(CO)_6L_2$ (L = Ph_2Ppy and t-dppv), $Co_2(CO)_6(dppa)$ and $Co_2(CO)_5(dpmp)$ where the ligands behave as mono-, di- and tridentate, respectively, via the ionic intermediates $[Co_2(CO)_3L_2][Co(CO)_4]$ (L = Ph_2Ppy and t-dppv) and $[Co(CO)_3 P\widehat{\ }P][Co(CO)_4]$ ($P\widehat{\ }P$ = dppa and dpmp). All the compounds have been characterized by elemental analysis, IR, electronic, ^1H and ^{31}P NMR spectroscopy.

Introduction

The reactions of dicobalt octacarbonyl with Lewis bases give rise to different products, depending on the nature of the base and reaction conditions. With monodentate phosphines the usual initial product is $[Co(CO)_{5-n}L_n][Co(CO)_4]$ [1], where the value of n is dependent on the base [2]; most usually $n = 2$. This salt can be converted to the dinuclear species, $Co_2(CO)_{8-n}L_n$ by heating in refluxing benzene. Much of the interest in the substitution reactions of cobalt carbonyls stems from modification of the hydroformylation catalyst $HCo(CO)_4$ with phosphine ligands [3]. With bis(tertiary phosphines) it yields complexes of the formula $Co_2(CO)_6(P\widehat{\ }P)$ [4]. Few of them have been characterized in the solid state and in solution [4, 5].

The present work describes the reactions of $Co_2(CO)_8$ with nucleophiles such as Ph_2Ppy, t-dppv, dppa and dpmp which can behave as mono-, bi- or tridentate ligands.

Experimental

All manipulations were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen. CH_2Cl_2 was dried over and distilled from P_4O_{10}. Hexane was dried over and distilled from sodium benzophenone ketyl.

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Dicobalt octacarbonyl was obtained from Fluka and used without further purification.

The reagents Ph_2Ppy [6], dppa [7], t-dppv [8] and dpmp [9] were prepared according to the literature and characterized by their IR and NMR spectra. The melting points and elemental analyses were in good agreement with the reported values.

Elemental analyses were performed by the Microanalytical Laboratory of this Department. The cobalt was determined by titration of the Co–EDTA complex in the presence of NET as indicator.

The IR spectra were recorded in the range $4000–200 \ cm^{-1}$ on a Nicolet 5DX FT-IR spectrometer using Nujol and hexachlorobutadiene mulls between CsI windows, KBr plates or in CH_2Cl_2 solution. ^1H and ^{31}P NMR spectra were obtained on a Bruker WH-200-SY instrument. All ^1H NMR chemical shifts are relative to TMS. ^{31}P chemical shifts are quoted relative to 85% H_3PO_4. The visible spectra were recorded on a Pye Unicam SP 8-100 ultraviolet spectrophotometer.

Preparation of $Co_2(CO)_6(Ph_2Ppy)_2$

To a 30 ml CH_2Cl_2 solution of $Co_2(CO)_8$ (2 g, 5.85 mmol) in a nitrogen-filled 100 ml Schlenk flask was added another solution of Ph_2Ppy (3.08 g, 0.012 mol) in the same solvent. An orange–red solid immediately appeared, and evolution of CO was observed. After 29 h, the reaction solution was filtered. The resulting orange–red solid was washed with cold n-hexane and dried under vacuum. The yield was 4.28 g (90%). *Anal.* Calc. for $C_{40}H_{28}N_2O_6P_2Co_2$: C, 59.08; H, 3.45; N, 3.45; Co, 14.51. Found: C, 59.02;

H, 3.38; N, 3.44; Co, 14.60%. ^{1}H NMR (CDCl$_3$): δ 7.12 (m, 5-py, 1H); 7.47 (m, 10H, C$_6$H$_5$); 7.82 (m, 3- and 4-py, 2H); 8.78 (m, 6-py, 1H). ^{31}P NMR (CDCl$_3$): δ 30.1 (s, coordinated P).

Preparation of Co$_2$(CO)$_6$(t-dppv)$_2$

By a similar procedure an orange solid was obtained from Co$_2$(CO)$_8$ (2 g, 5.85 mmol) and t-dppv (4.64 g, 0.012 mol). The yield was 5.62 g (89%). *Anal.* Calc. for C$_{58}$H$_{44}$O$_6$P$_4$Co$_2$: C, 64.52; H, 4.08; Co, 10.93. Found: C, 64.13; H, 3.95; Co, 10.80%. ^{1}H NMR (CDCl$_3$): δ 7.06 (s, br, 2H, CH=CH); 7.45 (m, *m*- and *p*-H, 12 H, C$_6$H$_5$); 7.80 (m, *o*-H, 8H, C$_6$H$_5$). ^{31}P NMR (CDCl$_3$): δ 24.4 (m, 1P, coordinated P); −5.5 (d, 1P, unligated P).

Preparation of Co$_2$(CO)$_6$(dppa)

By a similar procedure an orange solid was obtained from Co$_2$(CO)$_8$ (2 g, 5.85 mmol) and dppa (2.25 g, 5.85 mmol). The yield was 3.61 g (92%). This compound is also accessible in 30% yield by the procedure described in the literature [10]. *Anal.* Calc. for C$_{30}$H$_{21}$NO$_6$P$_2$Co$_2$: C, 53.63; H, 3.13; N, 2.08; Co, 17.56. Found: C, 53.41; H, 3.04; N, 2.12; Co, 17.48%. ^{1}H NMR (CDCl$_3$): δ 3.67 (t, 1H, NH); 7.40 (m, *m*- and *p*-H, 12H, C$_6$H$_5$); 7.43 (m, *o*-H, 8H, C$_6$H$_5$). ^{31}P NMR (CDCl$_3$): δ 105.2 (s, coordinated P).

Preparation of Co$_2$(CO)$_5$(dpmp)

By a similar procedure a brown solid was obtained from Co$_2$(CO)$_8$ (2 g, 5.85 mmol) and dpmp (2.96 g, 5.85 mmol). The yield was 3.58 g (80%). *Anal.* Calc. for C$_{37}$H$_{29}$O$_5$P$_3$Co$_2$: C, 58.08; H, 3.79; Co, 15.42. Found: C, 57.96; H, 3.77; Co, 15.32%. ^{1}H NMR (CDCl$_3$): δ 3.39 (m, 2H, CH$_2$); 3.66 (m, 2H, CH$_2$); 7.55 (m, 25H, C$_6$H$_5$). ^{31}P NMR (CDCl$_3$): δ 22.3 (d, 2P, coordinated terminal P); 28.6 (t, 1P, coordinated internal P).

Results and discussion

It is well-known that the reaction of certain phosphine and phosphite ligands with dicobalt octacarbonyl leads to rapid disproportionation [11]. In the case of these phosphines we find that the addition of L (L = Ph$_2$Ppy and t-dppv) to Co$_2$(CO)$_8$ gives rise to the anion [Co(CO)$_4$]$^-$, as is shown by the IR bands at 1885 cm^{-1} [12, 13], indicating that the formation of [Co(CO)$_3$L$_2$][Co(CO)$_4$] takes place. This reaction is rapid and is over in a matter of minutes.

The reaction to form the neutral dimers, Co$_2$(CO)$_6$(Ph$_2$Ppy)$_2$, Co$_2$(CO)$_6$(t-dppv)$_2$, Co$_2$(CO)$_6$-(dppa) and Co$_2$(CO)$_5$(dpmp) is much slower, again as monitored by infrared spectroscopy of the reaction mixture. The formation of disproportionation prod-

ucts suggests a radical chain mechanism involving electron transfer, analogous to that previously proposed [11, 14] for the reaction of Co$_2$(CO)$_8$ with P(n-Bu)$_3$.

All the compounds were characterized by means of elemental analysis, IR, ^{1}H and ^{31}P NMR spectra. Tables 1 and 2 contain the IR spectra of these complexes in the ranges 4000–3800, 2100–1700 and 600–400 cm^{-1}.

In all the compounds the bands corresponding to ν(P–C) [15] appear in the range 690–672 cm^{-1}.

In the complex Co$_2$(CO)$_6$(dppa) the vibration ν(NH) (3300 cm^{-1}) is shifted, as usual, toward higher energies relative to that for the free ligand (3225 cm^{-1}). This is attributed to a change in hybridization of the N atom from sp^3 to sp^2 [10, 16].

The spectra of these complexes in the carbonyl region are simple and indicate that Co$_2$(CO)$_6$L$_2$ (L = Ph$_2$Ppy and t-dppv) and Co$_2$(CO)$_5$(dpmp) have an unbridged structure and the complex Co$_2$(CO)$_6$(dppa) shows a bridged structure derived from Co$_2$(CO)$_8$ (C$_{2v}$ symmetry). This form is the

TABLE 1. IR spectra (cm^{-1}) in the ranges 4000–3800, 2100–1700 and 600–400 for Co$_2$(CO)$_6$L$_2$ complexes

Co$_2$(CO)$_6$(Ph$_2$Ppy)$_2$	Co$_2$(CO)$_6$(t-dppv)$_2$	Assignment	
CH$_2$Cl$_2$ solution			
2029w	2034w	A$_{1g}$	
1973s	1976s	A$_{2u}$	ν(CO)$_t$
1953vs	1954vs	E$_u$	
1924sh	1926sh	E$_g$	
Nujol			
3992vw	3998vw	A$_{1g}$ + A$_{2u}$	
3973w	3973w	A$_{1g}$ + E$_u$	
3898vw	3894vw	Eg + A$_{2u}$	
3855w	3863w	Eg + E$_u$	
CH$_2$Cl$_2$ solution			
548s	545s	A$_{2u}$	
515vs	517vs	E$_u$	δ(CoCO)
497s	498s	E$_u$	
475m	476m	A$_{2u}$	ν(CoC)
425m	423m	E$_u$	

TABLE 2. IR spectra (2100–1700 cm^{-1}) of Co$_2$(CO)$_6$(dppa) and Co$_2$(CO)$_5$(dpmp) complexes

Co$_2$(CO)$_6$(dppa)^a	Co$_2$(CO)$_5$(dpmp)^b	Assignment
2050vs (A$_1$0	2001vs	
2016vs (B$_1$)	1960vs	ν(CO)$_t$
1990vs (B$_2$)	1938vs	
1984sh (A$_2$)	1923s, sh	
1826m (A$_1$)		ν(CO)$_b$
1798s (B$_2$)		

^{a}In CH$_2$Cl solution.　^{b}In Nujol.

only one observed in CH_2Cl_2 solution as is shown by the IR spectra in the 300–180 °K temperature range.

Previous studies of the vibrational spectra of $Co_2(CO)_6L_2$ (L = PPh$_3$, P(n-Bu)$_3$, PEt$_3$, PMePh$_2$, PMe$_2$Ph) [17] and M[Co(CO)$_3$L]$_2$ (M = Hg, Cd; L = PEt$_3$, P(n-Bu)$_3$, PPh$_3$, PMePh$_2$) [18] have shown that these complexes probably have D_{3d} molecular symmetry; the results presented here are consistent with the assumption that the substituted compounds, $Co_2(CO)_6L_2$ (L = Ph$_2$Ppy and t-dppv) have the same symmetry with the ligands L occupying both axial coordination positions. The observed bands assigned to fundamental vibrations are designated in Table 1. These assignments are in agreement with the previously assigned [17, 18] infrared spectra of $Co_2(CO)_6L_2$ (L = PEt$_3$, PPh$_3$, PMePh$_2$) in these regions. The presence of four absorption bands due to combination modes in the spectra of $Co(CO)_6L_2$ (L = Ph$_2$Ppy and t-dppv) provides unequivocal evidence for a D_{3d} molecular symmetry.

The solution infrared spectrum for the dimer $Co_2(CO)_6$(dppa) is completely consistent with the structure shown schematically below, where the asymmetric and symmetric stretches of the bridging carbonyl groups present a small energy difference (only 20 cm^{-1}). This is the structure adopted by $Co_2(CO)_6$ (C$_4$F$_4$(AsMe)$_2$)$_2$) in the solid state [4, 19].
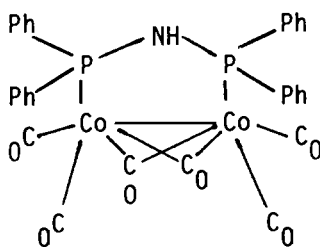
In the IR spectrum of $Co_2(CO)_5$(dpmp) the higher νCO absorption band (totally symmetric) falls in the range characteristic for trisubstituted derivatives and the spectrum is very similar to that of $Co_2(CO)_5$(PEt$_3$)$_3$ [20].

The force constants (Table 3) were calculated from the secular equations given by Manning and Miller [17b] and from the frequencies of the νCO vibrations. The force constants for $Co_2(CO)_6L_2$ (L = Ph$_2$Ppy and t-dppv) and $Co_2(CO)_6$(dppa) are essentially similar to those obtained for $Co_2(CO)_6L_2$ (L = PEt$_3$, P(n-Bu)$_3$, PEt$_2$Ph) [17b] and $Co_2(CO)_6$(acetylene) [21], respectively. The higher k_{Co} value for the $Co_2(CO)_6$(dppa) dimer is due to the presence of bridged carbonyls.

The ^{1}H and ^{31}P NMR spectra of these neutral dimers are reported in 'Experimental'. The usual downfield shift of the ^{31}P resonance is observed as the phosphorus coordinates to cobalt. For

TABLE 3. Force constants for $Co_2(CO)_6L_2$ (L = Ph$_2$Ppy and t-dppv) (D_{3d}) and $Co_2(CO)_6$(dppa) (C_{2v}) molecules (mdyn Å^{-1})[a]

L	k_{Co}	k_4	k_6	k_7
Ph$_2$Ppy	15.540	0.349	0.232	0.005
t-dppv	15.519	0.327	0.232	0.005
dppa	16.253	0.333	0.223	0.091

[a]k_{CO} is the C–O stretching force constant; k_4 is the interaction between cis-CO groups coordinated to the same metal atom; k_6 is the interaction between cisoid CO groups coordinated to different metal atoms; and k_7 is the interaction between transoid CO groups coordinated to different metal atoms.

TABLE 4. Electronic spectral data and transition assignments

Compound	Symmetry	$h\nu(\sigma \to \sigma^*)$ (kJ mol^{-1})
$Co_2(CO)_8$	D_{3d}	335
$Co_2(CO)_6$(Ph$_2$Ppy)$_2$	D_{3d}	305
$Co_2(CO)_6$(t-dppv)$_2$	D_{3d}	305
$Co_2(CO)_5$(dpmp)	D_{3d}	273
$Co_2(CO)_8$	C_{2v}	418
$Co_2(CO)_6$(dppa)	C_{2v}	392

$Co_2(CO)_6$(Ph$_2$Ppy)$_2$ one signal is observed in the range of coordinated P. For the complex $Co_2(CO)_6$(t-dppv)$_2$ two signals are observed in the ranges for coordinated P and uncoordinated P*. For the complex $Co_2(CO)_6$(dppa) the spectrum consists of a singlet significantly downfield shifted due to the equivalence of the two P-coordinated atoms. Finally in the case of the complex $Co_2(CO)_5$(dpmp) the spectrum shows a doublet and a triplet in the range for coordinated P indicating that the three P atoms are coordinated to the cobalt.

Electronic spectral data for the complexes in CH_2Cl_2 are shown in Table 4.. By analogy with other well-characterized dinuclear metal carbonyls, the absorption maximum at 305 and 273 kJ mol^{-1} for $Co_2(CO)_6L_2$ (L = Ph$_2$Ppy and t-dppv) and $Co_2(CO)_5$(dpmp), respectively (non-bridged form D_{3d} or D_{3h} symmetry) and at 392 kJ mol^{-1} for $Co_2(CO)_6$(dppa) (bridged form C_{2v}) are assigned to the $\sigma \to \sigma^*$ transition of the Co–Co bond in the non-bridged and bridged isomers, respectively [22]. The energy of the $\sigma \to \sigma^*$ transition depends on the nature of the substituent in ways that enable the importance of σ basicity, π acidity, and steric effects to be distinguished with some degree of clarity [22c]. The replacement of CO by phosphines results in an increased localization of dπ electron density on the Co atoms, which in turn would increase dπ–dπ

repulsive interactions and weaken the metal–metal bond [23]. The $\sigma \to \sigma^*$ transitions decrease in energy according to $Co_2(CO)_8 > Co_2(CO)_6L_2$ $Co_2(CO)_5$-(dpmp) $> (D_{3d}$ or D_{3h} symmetry) and $Co_2(CO)_8 > Co_2(CO)_6$(dppa) $(C_{2v}$ symmetry).

Acknowledgement

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