solution spectrum shows some concentration dependence. This is to be compared with the 238 p.p.m. observed by Mennitt *et al.* (1981) for hexakis-(imidazole)Cd^{II} in the solid state. Clearly, the species in methanol is not the species that exists in the solid state, and either the coordination sphere is expanded with one or more solvent molecules or some of the nitrogen ligands are replaced by solvent molecules. The former is the more likely since we have shown (Rodesiler, Griffith, Charles & Amma, 1985) a regular six-coordinate Cd species can readily add a seventh ligand to make the metal geometry seven-coordinate pentagonal bipyramidal. We have also shown that the addition of the oxygen donor from the solvent methanol shifts the ^{113}Cd NMR signal to more shielded values by approximately 70 p.p.m. (Rodesiler & Amma, 1982) as is observed in this case. However, the latter possibility cannot be completely ruled out because of the concentration dependence.

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Structures of Bis[tricarbonyl(trimethylphosphine)cobalt] (1) and Dicarbonylchlorobis(trimethylphosphine)cobalt (2)

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Abstract. (1), $[Co_2(CO)_6\{P(CH_3)_3\}_2]$, $M_r = 438\cdot08$, cubic, $Pa3$, $a = 12\cdot4539$ (18) Å, $V = 1931\cdot6$ Å^3, $Z = 4$, $D_x = 1\cdot507$ g cm^{-3}, $\lambda(\text{Mo }K\alpha) = 0\cdot71069$ Å, $\mu = 18\cdot977$ cm^{-1}, $F(000) = 888$, $T = 296$ (2) K, final $R = 0\cdot0272$ for 435 unique observations. The structure consists of discrete molecules of $[Co_2(CO)_6\{P(CH_3)_3\}_2]$. There is a Co—Co bond of $2\cdot669$ (1) Å. The geometry about each Co atom is trigonal bipyramidal with three equatorial carbonyls and an apical PMe$_3$ molecule *trans* to the other Co atom. (1) is a product of the reaction of $[Ni\{\mu\text{-}tert\text{-Bu(H)P}\}(PMe_3)_2]_2$ and $[Co_2(CO)_8]$ in toluene solution. (2),

$[CoCl(CO)_2\{P(CH_3)_3\}_2]$, $M_r = 302\cdot57$, orthorhombic, $Pnma$, $a = 9\cdot793$ (7), $b = 10\cdot602$ (4), $c = 13\cdot590$ (1) Å, $V = 1411\cdot2$ (2) Å^3, $Z = 4$, $D_x = 1\cdot424$ g cm^{-3}, $\lambda(\text{Mo }K\alpha) = 0\cdot71069$ Å, $\mu = 16\cdot06$ cm^{-1}, $F(000) = 624$, $T = 296$ (2) K, final $R = 0\cdot0512$ for 673 unique observed reflections. The structure of (2) has an overall trigonal-bipyramidal configuration with *trans* PMe$_3$ groups and two carbonyls and a Cl in the equatorial plane. The Cl and two CO groups which occupy the equatorial positions are disordered and the structure was refined successfully using partial occupancies of $\frac{1}{3}$ Cl, $\frac{2}{3}$ C and $\frac{2}{3}$ O at the appropriate sites. (2) is the product of the reaction of $(CO)_5Mo(tert\text{-Bu}_2P)Li$ with $[CoCl_2(PMe_3)_2]$ in THF at 183 K.

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Introduction. The solid-state structures of cobalt carbonyl complexes are of interest since many of these complexes are known to exhibit unusual catalytic properties. For example, the tri-n-butylphosphine complex $[Co_2(CO)_6(n\text{-}Bu_3P)_2]$ was shown to be an active hydroformylation catalyst having considerably different properties from those of bis(tetracarbonylcobalt) (Slaugh & Mullineaux, 1968). $[Co_2(CO)_6(n\text{-}Bu_3P)_2]$ was shown to be catalytically active at much lower pressures than $[Co_2(CO)_8]$ and to exert a much higher selectivity for alcohol production as the primary hydroformylation product. The structure of this compound was determined crystallographically by Ibers (1968). We obtained $[Co_2(CO)_6(PMe_3)_2]$ (1) from the reaction of $[Ni\{\mu\text{-}tert\text{-}Bu(H)P\}(PMe_3)_2]_2$ with $[Co_2\text{-}(CO)_8]$ (Jones, Norman, Seeberger, Atwood & Hunter, 1983) and have unequivocally determined its structure *via* X-ray crystallography.

In addition, although a number of five-coordinate Co^I species have been structurally characterized, the solid-state structure of $[CoCl(CO)_2(PMe_3)_2]$ (2) has never been unequivocally determined (Capelle, Dartiguenave, Dartiguenave & Beauchamp, 1983; Chiu, Wilkinson, Thornton-Pett & Hursthouse, 1984). A single-crystal X-ray structure of (2) was obtained to determine if the solid-state structure corresponded to the trigonal-bipyramidal geometry predicted by spectroscopy (Klein & Karsch, 1975).

Experimental. Red octahedral crystals of (1) and pale-yellow crystals of (2) were grown from hexane at 253 K and mounted in 0·5 mm thin-walled glass capillaries under N_2 (1 atm). Final lattice parameters determined from 25 strong reflections $(26 < 2\theta < 30°)$ carefully centered on an Enraf–Nonius CAD-4 diffractometer. Data collected by $\omega/2\theta$ scan technique. Details of crystal data and a summary of intensity-data-collection parameters for (1) and (2) are given in Table 1. For (1) the space group was uniquely defined by systematic absences $0kl, k = 2n + 1$, as $Pa3$. For (2) systematic absences $0kl, k + l = 2n + 1, hk0, h = 2n + 1$, indicated either $Pnma$ or $Pn2_1a$ as the space group. $Pnma$ was chosen on the basis of successful refinement. Data for (1) and (2) corrected for Lorentz and polarization effects. Absorption correction applied for (1) [but not for (2)] using an empirical ψ-scan method. Both structures solved using the $MULTAN$ direct-methods program (Germain, Main & Woolfson, 1971) for heavy atoms and successive cycles of full-matrix, least-squares refinement and difference Fourier maps using the Enraf–Nonius software package SDP–$Plus$ (Frenz and Associates, 1981) on a PDP 11/44 computer. Scattering factors from *International Tables for X-ray Crystallography* (1974), for all atoms in the neutral (0) oxidation state. A non-Poisson-contribution weighting scheme was used in both structures. This method uses an experimental

Table 1. *Crystal data and summary of intensity data collection and structure refinement for* (1) *and* (2)

	(1)	(2)
Crystal shape	Octahedral	Plate
Crystal size (mm)	0·14 (edge)	0·25 × 0·21 × 0·28
Absorption correction		
min. trans.	93·1179	None applied
max. trans.	99·8603	None applied
average value	95·7333	None applied
2θ range (°)	2·00 to 50·00	2·00 to 50·00
Scan width (°)	$0·8 + 35\tan\theta$	$0·8 + 0·35\tan\theta$
h,k,l range	0–14, 0–14, −14–14	0–11, 0–12, 0–16
Standard reflections	800, 008	$10\bar{6}, 4\bar{3}\bar{2}$
Decay of standards	0·8%	<2%
Reflections measured	3720	1459
Unique reflections observed		
$[I > 3\sigma(I)]$	435	673
No. parameters varied	50	93
Data/parameter ratio	8·700	7·237
R_{int}	$0·020(F_{obs})$	—
	0·025 (Intensity)	—
R	0·0272	0·0512
wR	0·0339	0·0671

instability factor (p) in the calculation of (I) to downweight intense reflections in the least-squares refinement. p values used were: (1) 0·02, (2) 0·03. {The function minimized in the least-squares refinement is $\sum w(|F_o| - |F_c|)^2$. Using the non-Poisson weighting scheme, w is given by the expression $4(F_o)^2/[\sigma(F_o)^2]^2$ where $[\sigma(F_o)^2]^2 = \{S^2(C + R^2B) + [p(F_o)^2]^2\}/Lp^2$ where S^2 is the scan rate squared, C is the total integrated peak count, R^2 is the ratio (squared) of scan time to background counting time, B is the total background count, Lp is the Lorentz–polarization factor.} H atoms located for (1) and refined isotropically. No chemically significant peaks present in final difference Fourier maps [max. peaks in final difference Fourier maps: (1) 0·241, (2) 0·644 e Å^{-3}, max. Δ/σ ratios: (1) 0·194, (2) 0·704].

Discussion. (1): A general view of the molecule is shown in Fig. 1. Atomic positional parameters are given in Table 2 with key bond lengths and angles in Table 3.* A threefold axis lies along the P–Co vector which generates the three carbonyl groups on Co from the unique C(1) and O positions as well as the three methyl C atoms on P from C(2). A crystallographic center of inversion lies midway between the two Co atoms generating Co' as well as the carbonyl and phosphine ligands bonded to it. The Co–Co' bond distance of 2·669 Å is quite similar to that of 2·66 Å found in $[Co_2(CO)_6(n\text{-}Bu_3P)_2]$ by Ibers (1968). The other bond lengths in the molecule are normal. There is a slight staggering of the phosphine methyl groups relative to

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42624 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the neighboring carbonyl groups, as shown by the angle of 15·5° between the planes Co—Co'—C(1)' and C(2)—P—Co.

(2): A general view of (2) is given in Fig. 2. Atomic positional parameters are given in Table 4 with key bond lengths and angles in Table 5. There is a crystallographically imposed mirror plane which passes through P(1), Co, C(12) and C(21) and which generates C(11)' from C(11) and C(22)' from C(22). Coordination of the two trimethylphosphine ligands in the *trans* axial sites minimizes steric interactions within the molecule. The Cl and two CO units which occupy the equatorial positions are disordered. The structure was refined successfully using partial occupancies of $\frac{1}{3}$ Cl, $\frac{2}{3}$ C and $\frac{2}{3}$ O at the appropriate sites. One of the

equatorial positions also lies in the mirror plane. The view shown in Fig. 2 has this position occupied by Cl(1). Thus C(1) and O(1) also generate C(1)' and O(1)' respectively *via* this plane. The bond lengths and angles all fall within normal limits.
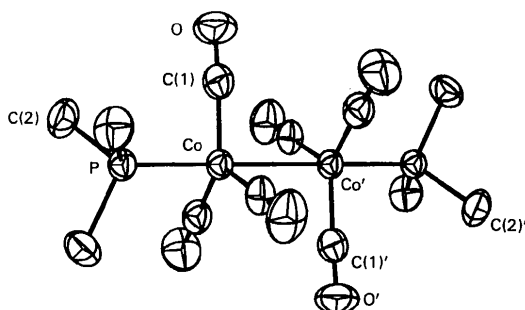

Fig. 2. A general view of [CoCl(CO)₂(PMe₃)₂] (2).

Fig. 1. A general view of [Co₂(CO)₆(PMe₃)₂] (1).

Table 2. *Positional and thermal parameters for* (1) *and their e.s.d.'s*

	x	y	z	B(Å²)
Co	0·06191 (3)	0·06191	0·06191	2·754 (3)
P	0·16281 (6)	0·16281	0·16281	2·911 (7)
O	0·2216 (2)	0·0567 (2)	−0·1086 (2)	6·00 (7)
C(1)	0·1573 (3)	0·0575 (3)	−0·0436 (3)	3·77 (7)
C(2)	0·1692 (3)	0·3024 (3)	0·1226 (3)	4·54 (8)
H(1)	0·339 (2)	0·172 (3)	0·209 (2)	4·9 (8)*
H(2)	0·130 (3)	0·091 (3)	0·335 (3)	5·9 (9)*
H(3)	0·197 (3)	0·306 (3)	0·053 (3)	8 (1)*

Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the equivalent isotropic thermal parameter defined as: $\frac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table 4. *Positional and thermal parameters for* (2) *and their e.s.d.'s*

	x	y	z	B(Å²)
Co	0·2947 (2)	0·250	0·0243 (1)	2·83 (3)
Cl(1)	0·439 (1)	0·250	−0·1120 (8)	5·8 (3)*
P(1)	0·1224 (4)	0·250	−0·0797 (3)	3·57 (8)
P(2)	0·4733 (3)	0·250	0·1211 (3)	3·31 (7)
O(1)	0·204 (1)	0·486 (1)	0·1124 (8)	7·1 (3)*
C(1)	0·238 (1)	0·395 (1)	0·083 (1)	3·3 (3)*
C(11)	0·118 (1)	0·3850 (9)	−0·1640 (7)	5·1 (2)
C(12)	−0·047 (1)	0·250	−0·024 (1)	4·9 (3)
C(21)	0·433 (1)	0·250	0·250 (1)	5·3 (4)
C(22)	0·5847 (9)	0·386 (1)	0·1044 (8)	6·4 (3)
Cl(2)	0·2119 (7)	0·4348 (7)	0·0941 (5)	4·3 (2)*
O(2)	0·485 (2)	0·250	−0·137 (1)	8·2 (5)*
C(2)	0·406 (2)	0·250	−0·071 (1)	5·4 (6)*

Anisotropically refined atoms are given in the form of the equivalent isotropic thermal parameter defined as: $\frac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$. Starred atoms were disordered in the equatorial plane about the threefold axis. Successful refinement was achieved using the following fixed partial occupancies: Cl(1) = 0·17, O(1) = 0·66, C(1) = 0·66, Cl(2) = 0·33, O(2) = 0·33, C(2) = 0·33.

Table 3. *Interatomic distances* (Å) *and angles* (°) *for* (1) *with e.s.d.'s in parentheses*

Co—Co'	2·669 (1)	C(2)—H(1)	0·92 (3)
Co—C(1)	1·772 (3)	C(2)—H(2)	1·06 (3)
Co—P	2·175 (1)	C(2)—H(3)	0·93 (3)
C(1)—O	1·139 (3)		
P—C(2)	1·810 (3)		

Co—Co'—P	180·00	Co—P—C(2)	114·9 (1)
Co—Co'—C(1)	86·668 (8)	C(2)—P—C(2)'	103·6 (1)
P—Co—C(1)	93·34 (8)	Co—C(1)—O	177·2 (2)
C(1)—Co—C(1)'	119·67 (2)	P—C(2)—H(1)	109 (2)

Table 5. *Interatomic distances* (Å) *and key bond angles* (°) *for* (2) *with e.s.d.'s in parentheses*

Co—Cl(1)	2·33 (2)	P(1)—C(11)	1·834 (6)
Co—P(1)	2·200 (3)	P(1)—C(12)	1·820 (9)
Co—P(2)	2·189 (3)	P(2)—C(21)	1·795 (3)
Co—C(1)	1·82 (3)	P(2)—C(22)	1·822 (7)
Co—Cl(2)	2·323 (11)	O(1)—C(1)	1·09 (3)
Co—C(2)	1·69 (3)	O(2)—C(2)	1·18 (5)

Cl(1)—Co—P(1)	87·4 (6)	C(1)—Co—C(1)'	115·0 (3)
Cl(1)—Co—C(1)	122·0 (1)	C(11)—P(1)—C(11)'	102·6 (4)
P(1)—Co—P(2)	177·0 (1)	C(11)—P(1)—C(12)	103·9 (3)
P(1)—Co—C(1)	93·0 (1)		

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Structure of the 1:2 Complex of Cobalt(II) with 2,3-Naphthosemiquinone Diimine Anion

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Abstract. $[Co(C_{10}H_8N_2)_2]$, $M_r = 371 \cdot 31$, triclinic, $P\bar{1}$, $a = 5 \cdot 813$ (3), $b = 7 \cdot 8818$ (9), $c = 16 \cdot 985$ (2) Å, $\alpha = 84 \cdot 61$ (1), $\beta = 83 \cdot 83$ (2), $\gamma = 85 \cdot 65$ (3)°, $V = 768 \cdot 58$ Å^3, $Z = 2$, $D_m = 1 \cdot 60$, $D_x = 1 \cdot 60$ Mg m^{-3}, $\lambda(Mo\,K\alpha) = 0 \cdot 7093$ Å, $\mu = 1 \cdot 122$ mm^{-1}, $F(000) = 382$, $T = 298$ K, final $R = 0 \cdot 041$ for 2036 observed reflections. The unit cell contains two independent molecules, each lying on a crystallographic inversion center. The complex molecules are nearly planar and packed in a parallel fashion along the a axis. The structure reveals the delocalized bond pattern of the 2,3-naphthosemiquinone diimine anion ligand.

Introduction. It is particularly interesting that the transition-metal complexes with highly delocalized unsaturated electron-rich ligands have unusual properties; they are intensely colored, have an extensive electrochemistry (Balch & Holm, 1966), and possibly contain metal–metal bonds (Peng & Goedken, 1976; Peng, Liaw, Wang & Simon, 1985). The extent of π-electron delocalization over the unsaturated electron-rich ligand moiety is also a novel structural property. Examples of this type are metal complexes of dithiene (Teo & Snyder-Robinson, 1979), o-benzoquinone diimine anion (bqdi) (Hall & Soderberg, 1968; Christoph & Goedken, 1973; Peng, Chen, Liaw, Chen

& Wang, 1985), diiminosuccinonitrilo anion (Peng, Wang & Chiang, 1984; Peng, Liaw, Wang & Simon, 1985), and macrocyclic anions (Peng & Goedken, 1976; Peng, Ibers, Miller & Holm, 1976).

2,3-Naphthalenediamine can be oxidized under basic conditions to form 2,3-naphthosemiquinone diimine anion (s-nqdi) and 2,3-naphthoquinone diimine (nqdi).

s-nqdi   nqdi
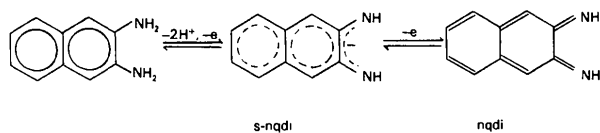
The title complex was synthesized by air oxidation of 2,3-naphthalenediamine and cobalt(II) acetate in *N,N*-dimethylformamide (DMF) solution. The structure was determined in order to elucidate the structural properties of the s-nqdi ligand.

Experimental. Crystals of $[Co(s\text{-nqdi})_2]$ obtained by slow formation of the complex in DMF solution. Crystal $0 \cdot 02 \times 0 \cdot 1 \times 0 \cdot 7$ mm. CAD-4 diffractometer. D_m measured by flotation. Absorption correction according to the experimental ψ rotation. $2\theta_{max} = 60°$ ($0 \le h \le 8$, $-11 \le k \le 11$, $-23 \le l \le 23$). Unit cell: least-squares refinement of 25 reflections ($15 < 2\theta < 25°$). Three standard reflections, <2% variation. 4864

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