

Complexes of Long-Chain Bidentate Ligands: Cobalt(II), Nickel(II), Rhodium(I) and Iridium(I) with α , ω -Bis(diphenylphosphino)alkanes, and Palladium(II) and Platinum(II) with 1,10-Bis(ethylthio)decane^{*}

R. V. PARISH* and S. M. RAZZOKI

Department of Chemistry, The University of Manchester Institute of Science and Technology, Manchester, M60 1QD, U.K.

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Abstract

Complexes of the ligands $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 8, 10$, or 16) with cobalt(II), nickel(II), rhodium(I) and iridium(I), and of $\text{EtS}(\text{CH}_2)_{10}\text{SEt}$ with palladium(II) and platinum(II) have been characterised. The cobalt(II) complexes are tetrahedral, and the nickel(II) complexes planar, both sets being dimeric $[\text{MX}_2(\text{L}-\text{L})]_2$ with bridging ligands forming $(2n + 6)$ -membered rings. Rhodium(I) and iridium(I) form carbonyl complexes $[\text{MX}(\text{L})(\text{L}-\text{L})]_2$ ($\text{L} = \text{CO}$) which are also dimeric; low-temperature ^{31}P NMR studies show the presence of two conformers. The corresponding complexes with $\text{L} = \text{PPh}_3$ appear to lose the monodentate phosphine in solution but probably remain dimeric; they may contain three-coordinate rhodium(I). In contrast, the complexes $[\text{MX}_2(\text{EtS}(\text{CH}_2)_{10}\text{SEt})]$ ($\text{M} = \text{Pd}$ or Pt) are monomeric, with the chelating ligand occupying *trans* positions.

Introduction

Bidentate ligands can coordinate in a variety of ways. When the donor atoms are joined by a short chain (2–4 links), *cis*-chelation is normal. Long-chain ligands, which have become popular in recent years, may chelate to *trans* positions or may bridge to give oligomeric macrocyclic systems. The factors influencing the type of product formed have been reviewed recently [1]. For palladium(II) and platinum(II), for which the basic coordination geometry of the metal is not in doubt, the chain-length appears to be the most important factor: polymeric species are favoured by relatively short chains (*ca.* 6 links), cyclic dimers are found with 8–10 links, and *trans*-bonded monomers result with long chains (*ca.* 16 links). We report now on complexes of these metals with the long-chain dithioether

ligand $\text{EtS}(\text{CH}_2)_{10}\text{SEt}$ (etd), and also on complexes of intermediate- and long-chain diphosphines $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ [$n = 8$ (dpo), 10 (dpd) or 16 (dphd)] with cobalt(II), nickel(II), rhodium(I), and iridium(I).

Experimental

Spectroscopic data were obtained with the following spectrometers: infrared, Perkin-Elmer 621 and Beckman IR72; electronic, Beckman Acta IV; ^1H NMR, Perkin-Elmer-Hitachi R20, Perkin-Elmer R32; ^{31}P NMR, Bruker WP80; mass, AEI MS902. Molecular weights were determined in chloroform on a Beckman-Hitachi osmometer. Magnetic moments were measured by the Faraday method by Mr. S. Chapman, to whom we are grateful.

The ligands were prepared by standard methods [2, 3], and characterised by chemical analysis and mass spectrometry. The complexes were obtained by methods of which the following are typical.

1,8-Bis(diphenylphosphino)octanedichlorocobalt(II), $[\text{CoCl}_2(\text{dpo})]_2$

Cobalt(II) chloride hexahydrate (0.13 g, 1.0 mmol) was dissolved in the minimum amount of ethanol. A solution of the ligand (0.48 g, 1.0 mmol) in hot ethanol (20 cm^3) was added dropwise. The mixture was refluxed gently for one hour. The resulting blue precipitate was filtered off, washed with ethanol and diethyl ether, and dried *in vacuo*. Yield, 85%.

1,10-Bis(diphenylphosphino)decanedichloronickel(II), $[(\text{NiCl}_2(\text{dpd}))_2]$

Nickel(II) chloride hexahydrate (0.64 g, 1.0 mmol) was dissolved in ethanol (50 cm^3). A solution of the ligand (1.5 g, 1.0 mmol) in ethanol (50 cm^3) was added dropwise, and the mixture was stirred for half an hour. The volume was then reduced to half, when a dark-red precipitate formed and was filtered off. The precipitate was washed with ethanol and diethylether, and dried *in vacuo*. Yield, 87%.

* Author to whom correspondence should be addressed.

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1,10-Bis(diphenylphosphino)decanecarbonylchlororhodium(I), [RhCl(CO)(dpd)]₂

The complex [RhCl(CO)(PPh₃)₂] (0.70 g, 1.0 mmol) was dissolved in dichloromethane (20 cm³) and the ligand (0.51 g, 1.0 mmol) in dichloromethane (10 cm³) was added dropwise over one hour. The product was precipitated by filtering the solution into six times its volume of petroleum ether (BP 40–60 °C). An atmosphere of carbon monoxide or nitrogen was maintained at all times. Yield, 61%.

1,10-Bis(diphenylphosphino)decanechloro(triphenylphosphine)rhodium(I), [RhCl(PPh₃)(dpd)]₂

To a solution of [RhCl(PPh₃)₃] (0.92 g, 1.0 mmol) in ethanol (20 cm³) was added dropwise a solution of the ligand (0.50 g, 1.0 mmol) in hot ethanol (25 cm³), and the mixture was refluxed gently for a further hour. The red-brown solid product was filtered off, washed with ethanol and diethylether, and dried *in vacuo*. Yield, 54%.

1,10-Bis(ethylthio)decanedichloropalladium(II), [PdCl₂(etd)]

Sodium tetrachloropalladate(II) (0.262 g, 1.00 mmol) was dissolved in ethanol (50 cm³) and a solution of the ligand (0.26 g, 1.0 mmol) in dichloromethane (50 cm³) was added slowly with stirring. A pink precipitate formed instantly. On heating, the solid slowly redissolved to give a pale yellow solution which was refluxed gently for three hours, filtered and evaporated to dryness. The oily product was dissolved in dichloromethane, filtered, and concentrated to 10 cm³. After long standing, the pale yellow complex precipitated, was filtered off, washed with ethanol and diethylether and dried. Yield, 80%.

Results and Discussion

Cobalt(II) Complexes

On stirring ethanolic solutions of cobalt(II) halides and dpo or dpd, the complexes CoX₂(L–L) (X = Cl, blue; Br, light green) were formed, analytical and physical data for which are given in Table I.

The molecular-weight determinations show that the complexes are accurately dimeric. The visible spectra are characteristic of pseudo-tetrahedral geometry, and are very similar to those of related

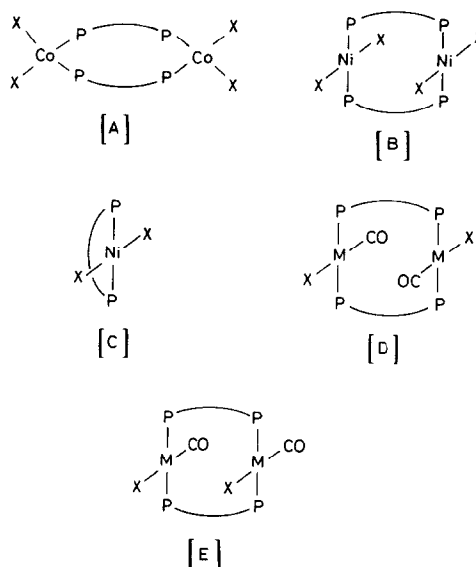


TABLE I. Data for Cobalt(II) Complexes CoX₂(L–L).

	L–L = dpo		L–L = dpd	
	X = Cl	X = Br	X = Cl	X = Br
% C	62.9(62.6)	54.4(54.7)	63.4(63.7)	55.1(55.9)
% H	6.0(5.8)	5.5(5.1)	6.2(6.2)	5.6(5.4)
% X	10.5(11.0)	22.2(22.7)	11.1(11.0)	21.7(21.9)
% P	9.4(10.1)	8.4(8.8)	9.4(9.6)	8.0(8.4)
RMM ^a	1220(1224)	1403(1403)	1268(1279)	1463(1457)
E _{max} ^b	14.1(473)	13.3(730)	13.8(400)	13.0(537)
10 ³ cm ⁻¹	15.5(630)	15.1(1020)	15.3(650)	14.7(838)
	16.8(560)	15.6(930)	16.1(612)	15.6(766)
E _{max} ^c	13.6	13.6	13.8	13.4
10 ³ cm ⁻¹	15.3	15.1	15.0	14.9
	15.7	15.9	15.9	15.6
μ _{eff} /μ _B	4.38	4.46	4.33	4.49
ν(Co–X)	334	274	344	265
cm ⁻¹	305	240	310	230

^a Figures in parentheses are calculated dimeric formula weights. ^b 10⁻³ mol dm⁻³ in CHCl₃. Figures in parentheses are ε_{mol}/dm³ mol⁻¹ cm⁻¹. ^c By reflectance.

^b 10⁻³ mol dm⁻³ in CHCl₃. Figures in parentheses are ε_{mol}/

TABLE II. Data for Nickel(II) Complexes NiX₂(L-L).

	L-L = dpo			NCS	L-L = dpd			NCS
	X = Cl	Br	I		Cl	Br	I	
% C	61.7(61.4)	55.0(55.4)	48.3(48.2)	62.1(62.0)	63.8(63.6)	56.0(56.3)	49.6(49.5)	63.1(63.0)
% H	5.8(6.0)	5.1(5.6)	4.5(5.0)	5.4(5.3)	6.2(5.7)	5.4(5.6)	4.8(4.1)	5.0(5.8)
% Br or N		22.8(22.6)		4.2(4.5)		21.9(21.8)		4.1(4.3)
RMM ^a				1182(657)				1164(685)
E _{max} ^b	18.2(90)	17.2(67)	15.8(26)	25.5(126)	18.1(87)	18.1(64)	16.8(30)	25.5(126)
10 ³ cm ⁻¹	25.0(930)	23.8(288)	20.0(198)	32.4(1740)	24.6(1090)	22.7(838)	21.9(240)	31.9(1780)
E _{max} ^c	18.8	17.5	14.6	25.3	19.2	17.5	16.6	25.6
10 ³ cm ⁻¹	25.0	24.1	20.0	32.4	25.0	23.9	19.6	32.4
$\nu(\text{Ni-X})$	339	262	230		337	258	220	
$\nu(\text{Ni-P})$	250	230			247	232		
$\nu(\text{C-N})$				2090				2090
$\nu(\text{C-S})$								861
cm ⁻¹				875				

^a Figures in parenthesis are the calculated monomer formula weights.^b 10⁻³ mol dm⁻³ in CHCl₃; figures in parenthesis are $\epsilon_{\text{mol/dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}}$.^c By reflectance.

complexes containing two monodentate tertiary phosphine ligands [4, 5]. The tetrahedral stereochemistry is confirmed by the magnetic moments: 4.33–4.49 μ_B at ambient temperature.

These complexes are therefore 22- and 26-membered ring systems involving tetrahedral cobalt(II) [A].

Nickel(II) Complexes

Rapid reaction occurred when dpo or dpd was added to ethanolic solutions of nickel(II) halides, giving highly coloured precipitates of the complexes $NiX_2(L-L)$ ($X = Cl$, purple; Br , green; I , rust; NCS , orange). Analytical and physical data are given in Table II.

The solids are diamagnetic, indicating square-planar geometry which is supported by the visible spectra of both the solids and their solutions. The infra-red spectra show single, unsplit bands for $\nu(Ni-X)$ and $\nu(Ni-P)$, indicative of *trans* stereochemistry. The data for the two thiocyanate complexes are consistent with binding of the anion through nitrogen [6, 7]. The occurrence of single bands for $\nu(C-N)$ again suggests *trans* geometry.

Unfortunately, most of the nickel(II) complexes were insufficiently soluble for accurate molecular-weight measurements to be obtained. The two thiocyanates gave molecular weights 70–80% higher than expected for monomers, suggesting that these complexes exist in solution predominantly as the dimers [B], in equilibrium with some monomer. Similar behaviour has been noted for analogous palladium(II) [8] and platinum(II) [9] complexes. The insolubility of the halide derivatives may indicate higher degrees of polymerisation.

There is thus a contrast between the dpo and dpd complexes of nickel(II) and cobalt(II), in that the latter are exclusively dimeric. The greater ease of formation of the monomer in the case of nickel(II)

is probably related to the increase in bond angle at the metal to 180° which can better accommodate the lengthy ligands.

Rhodium(I) and Iridium(I) Carbonyl Complexes

When the complexes $[MX(CO)(PPh_3)_2]$ ($M = Rh, Ir$; $X = Cl, Br$) were refluxed in ethanol with an excess of a diphosphine ligand, the pale-yellow complexes $MX(CO)(L-L)$ were isolated [$(L-L) = dpd, dpd$]. Data for these complexes are presented in Table III.

The NMR data show that all phosphorus atoms are equivalent, suggesting *trans* coordination. This is confirmed for the rhodium complexes by the magnitude of the $^{31}P-^{103}Rh$ coupling constants (111–112 Hz), which are in the same range as those reported for other *trans*-P–Rh–P systems [10–12] and show no evidence of the higher values characteristic of *trans*-P–Rh–CO [11]. Similarly, the infra-red data are comparable with those for a variety of *trans*- $MX(CO)L_2$ complexes with monodentate or bridging bidentate phosphine ligands [11, 13–17], and single absorptions are found for the M–X and C–O groups.

Molecular-weight data suggest that the complexes are essentially dimeric, so that the ligands are again bridging. In this case, two structural isomers are possible [11, 12, 18, 19], with the CO groups *cis* or *trans* with respect to the macrocyclic ring [D or E]. Since the ligand backbones are long, the metal-centred units will be so separated that vibrational coupling between them is unlikely; it is therefore not possible to use the IR data to support structure [D]. When solutions were cooled to 193 K, the ^{31}P NMR spectra exhibited two doublets of approximately equal intensity, suggesting that both isomers were present. At room temperature interconversion is rapid, presumably by rotation about the P–M–P axes. The alternative possibility, a rapidly exchanging mixture of monomer and dimer, is ruled out by the observation of Rh–P nuclear spin coupling at room

TABLE III. Data for Rhodium(I) and Iridium(I) Carbonyl Complexes $MX(CO)(L-L)$.

	RhCl(CO)(dpd)	RhBr(CO)(dpd)	RhCl(CO)(dpd)	IrCl(CO)(dpd)	IrBr(CO)(dpd)
%C	56.0(56.8)	58.5(58.2)	63.8(63.1)	55.0(54.8)	51.5(51.8)
%H	4.8(5.0)	5.7(5.5)	7.0(6.8)	5.7(5.2)	4.6(4.9)
%P	9.6(9.2)	8.7(8.6)	8.6(8.1)	7.6(8.1)	7.0(7.6)
%X	5.0(5.2)		5.0(4.7)	5.1(4.6)	
RMM	1268(676)	1281(721)	1422(760)	1026(766)	1463(810)
$\nu(C-O)/cm^{-1}$ ^a	1975	1955	1970	1975	1965
$\nu(M-X)/cm^{-1}$	310	220	305	302	252
$\delta(^{31}P)$ ^b	27.1 ^d	26.0	28.1 ^f	26.3	21.0
$^1J(Rh-P)/Hz$	111.0 ^e	109.8	112.8 ^g		
$\delta_{cp} - \delta_{L-L}$	11.9	10.8	12.4	11.1	5.8

^aIn $CHCl_3$. ^bIn $CDCl_3$, ppm to high frequency of 85% H_3PO_4 , at ambient temperature. ^cCoordination chemical shift, ppm. ^d29.7 and 28.1 at 193 K. ^e110.1 and 125.8 at 193 K. ^f27.9 and 26.5 at 193 K. ^g112.9 and 126.7 at 193 K.

TABLE IV. C—O Stretching Frequencies for $\text{MX}_3(\text{CO})(\text{L}-\text{L})$.

M	L—L	X	$\nu(\text{C}-\text{O})/\text{cm}^{-1}$
Rh	dph	Cl	2065
	dph	Br	2050
	dphd	Cl	2070
Ir	dph	Cl	2070
	dphd	Br	2060

temperature; formation of the monomer from the ligand-bridged dimer would require breaking of the Rh—P bonds with consequent loss of coupling.

When solutions of these complexes were treated with halogens, the C—O stretching frequencies were observed to increase, showing that oxidative-addition had occurred to give $\text{MX}_3(\text{CO})(\text{L}-\text{L})$ (Table IV); these products were not isolated.

Other Rhodium(I) Complexes

When the complexes $\text{RhX}(\text{PPh}_3)_3$ (X = Cl, Br) were refluxed in chloroform with the bidentate phosphines, pale orange products were isolated which analysed as $\text{RhX}(\text{PPh}_3)(\text{L}-\text{L})$ (Table V); in one case a product containing no triphenylphosphine was obtained, $\text{RhCl}(\text{dpo})$.

The molecular weights are all higher than required for monomers, but none is as large as the dimer value, suggesting some dissociation of an essentially dimeric species, possibly by loss of PPh_3 . This was confirmed by the ^{31}P NMR spectra which, at ambient temperature, showed a doublet [$^1J(\text{Rh}-\text{P})$ ca. 110 Hz] and a singlet to higher frequency. The latter signals were close to the position expected for free triphenylphosphine, suggesting a dissociation similar to that observed for $\text{RhCl}(\text{PPh}_3)_3$ [10]. The complexes may be essentially three-coordinate or a solvent molecule may be bound in place of the dissociated PPh_3 . A three-coordinate intermediate of the type $[\text{RhCl}\{\text{Bu}_2^t\text{P}(\text{CH}_2)_5\text{PBu}_2^t\}]_2$ has been postulated in the interconversion of the structural isomers of $[\text{Rh}(\text{H})\text{Cl}\{\text{Bu}_2^t\text{P}(\text{CH}_2)_5\text{PBu}_2^t\}]_2$ [12, 20]. At low

temperatures two signals are seen in the NMR spectrum corresponding to the coordinated phosphine, as with the carbonyl complexes; a similar isomerism is expected.

Palladium(II) and Platinum(II) Complexes

The reaction of etd with $\text{K}_2[\text{MCl}_4]$ (M = Pd, Pt) in aqueous ethanol results in the rapid formation of a pink precipitate which redissolves on heating to give pale yellow solutions yielding on evaporation the complexes $[\text{MCl}_2(\text{etd})]$. The initial precipitates are presumably the Magnus salts $[\text{M}(\text{etd})_2][\text{MCl}_4]$, similar to those observed by other workers with thioether and dithioether ligands [3, 21, 22].

The final products are monomeric in chloroform. The electronic spectra are consistent with the expected planar stereochemistry, and are similar to those of other dithioether complexes [3]; there is no evidence of association in the solid state [23]. The far IR spectra show single bands assigned to M—Cl and M—S stretching modes, suggesting *trans* geometry. The complexes are therefore analogous to those of $\text{PhS}(\text{CH}_2)_{12}\text{SPh}$ rather than $\text{PhS}(\text{CH}_2)_n\text{SPh}$ (n = 6, 8) [3].

Conclusion

The diphosphines $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ used here (n = 8, 10) give bridged dimeric complexes with cobalt(II), rhodium(I) and iridium(I). In all cases except the first, the metals are in square planar coordination. The behaviour of rhodium(I) and iridium(I) are similar to the isoelectronic *trans*-palladium(II) and -platinum(II) complexes, which also give dimeric species with ligands having n = 8–16 when the donor group is Ph_2P - or Ph_2As - [8, 9, 23]. For Bu_2^tP -ligands, dimeric complexes are found for n = 5–8, and longer chains (up to 12) give *trans*-bonded monomers [20, 23–26].

The behaviour of the nickel(II) system appears to be very dependent on the details of ligand structure and experimental conditions. For the ligands

TABLE V. Data for Rhodium(I) Complexes.

	$\text{RhCl}(\text{PPh}_3)(\text{dph})$	$\text{RhBr}(\text{PPh}_3)(\text{dph})$	$\text{RhCl}(\text{PPh}_3)(\text{dphd})$	$\text{RhCl}(\text{dpo})$
%C	68.8(68.5)	65.9(65.3)	69.1(69.9)	61.8(61.8)
%H	6.0(6.0)	5.0(5.8)	6.5(6.7)	5.8(5.7)
%P	7.0(10.2)	9.0(9.7)	9.8(9.3)	10.0(10.0)
%X				5.0(5.7)
RMM	1017(910)	1808(955)	1268(994)	1080(621)
$\nu(\text{Rh}-\text{X})/\text{cm}^{-1}$	300	232	295	298
$\delta(^{31}\text{P})^a$	27.9 ^b	27.0 ^b	28.1 ^{b,c}	28.1 ^d , 29.7 ^d
$^1J(\text{Rh}-\text{P})/\text{Hz}$	111.9	108.0	112.9 ^c	125.8 ^d , 110.1 ^d

^a In CDCl_3 , ppm to high frequency of 85% H_3PO_4 , at ambient temperature. K: 27.8 and 25.9 ppm, 112.7 and 111.8 Hz.

^b Also shows singlet at ca. -7 ppm.

^c At 193

^d At 193 K.

TABLE VI. Data for Palladium(II) and Platinum(II) Complexes MX₂(etd).

	M = Pt		M = Pd	
	X = Cl	X = Br	X = Cl	X = Br
%C	31.0(31.8)	27.9(27.2)	39.0(38.2)	32.0(31.9)
%H	5.8(5.6)	4.8(4.8)	7.4(6.8)	5.6(5.6)
%X	14.0(13.4)	26.0(25.9)	15.6(16.1)	
%S		10.3(10.6)		11.9(12.1)
RMM	517(528)	678(617)	506(439)	479(528)
E _{max} /10 ³ cm ⁻¹ ^a	27.0(3690)	25.2(12320)	23.0(450)	21.8(570)
	30.3(4030)	29.2(870)	26.3(2770)	24.3(1260)
	33.4(5020)	33.4(1510)	30.3(7300)	30.3(4430)
E _{max} /10 ³ cm ⁻¹ ^b	25.7	24.4	24.1	23.6
	30.3	30.3	26.3	30.6
	37.2	33.9	31.3	
ν(M-X)/cm ⁻¹	360	270	356	268
ν(M-S)/cm ⁻¹	300	320	298	318

^a In CHCl₃; figures in parentheses are ε_{mol}/dm³ mol⁻¹ cm⁻¹. ^b By reflectance.

Ph₂P(CH₂)_nPPh₂ (n = 4, 5) and Ph₂P(CH₂)₂O(CH₂)₂-PPh₂, the halides (Cl, Br) give monomeric tetrahedral complexes, while the thiocyanates are planar [27, 28]. For Ph₂P(CH₂)₂O(CH₂)₂O(CH₂)₂PPh₂ (poop), which is analogous to dpo, the complexes are all monomeric, the chloride and bromide being tetrahedral in the solid state while the iodide and thiocyanate are planar; in solution, all appear to be planar [29, 30]. A diamagnetic toluene solvate of the bromide has been isolated [28]. We find the dpo complexes to be principally dimeric in solution, and to be planar. It is possible that, as with poop, differences in solvent may play a part in determining the stereochemistry of the dpo complexes; other workers report that dimeric tetrahedral complexes are formed from anhydrous nickel halides and the ligand in n-butanol [31].

The only simple monomeric complexes to be obtained were the palladium(II) and platinum(II) halide derivatives of EtS(CH₂)₁₀SEt, which are analogous to previously reported complexes of PhS(CH₂)₁₂SPh; shorter ligands give polymeric derivatives [3].

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