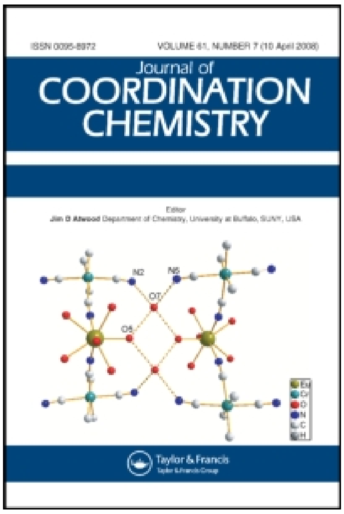

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SYNTHESIS, CHARACTERIZATION AND REACTIVITIES OF DINUCLEAR RHODIUM(I) COMPLEXES OF A HEXADENTATE LIGAND, *N,N,N',N'-TETRAKIS* [2-(DIPHENYLPHOSPHINO) ETHYL] ETHANE-1,2-DIAMINE

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SYNTHESIS, CHARACTERIZATION AND REACTIVITIES OF DINUCLEAR RHODIUM(I) COMPLEXES OF A HEXADENTATE LIGAND, *N,N,N′,N′-TETRAKIS* [2-(DIPHENYLPHOSPHINO) ETHYL] ETHANE-1,2-DIAMINE

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A number of square planar dinuclear rhodium(I) complexes, $[Rh_2LX_2]$ (X=Cl, I, N_3) and $[Rh_2L][ClO_4]_2$ have been prepared with a hexadentate ligand having N_2P_4 donor sites, *N,N,N′,N′-tetrakis*[2 - (diphenylphosphino) ethyl]ethane-1,2-diamine (L). The compound $[Rh_2LCl_2]$ readily undergo oxidative addition reactions with Cl_2, Br_2, I_2 and MeI which result in the formation of octahedral dinuclear complexes with additional ligands in axial positions. $[Rh_2LCl_2]$ with $NOBF_4$ forms a pentacoordinate complex $[Rh_2L(NO)_2Cl_2][BF_4]_2$. Reaction of $[Rh_2LX_2]$ (X=Cl,N_3) with CO gives pentacoordinate dinuclear complexes $[Rh_2L(CO)_2X_2]$ with trigonal bipyramidal geometry. However, a CO adduct $[Rh_2L(CO)_4I]_2$ is obtained when $[Rh(cod)I]_2$ reacts with L in CO-saturated dichloromethane solution. All CO adducts react with O_2 to give octahedral carbonato complexes, $[Rh_2L(O)_4(CO_3)_2X_2]$ (X=Cl, I, N_3) in which CO_3^{2-} acts as a bidentate ligand and PPh_2 of L is oxidised to $Ph_2P{=}O$ which coordinates to rhodium through oxygen. The complex $[Rh_2LCl_2]$ reacts with SO_2 to give $[Rh_2L(SO_2)_2Cl_2]$ which on reaction with O_2 results in the formation of the octahedral sulphato complex $[Rh_2L(O)_4(SO_4)_2Cl_2]$. Reaction of $[Rh_2LCl_2]$ with O_2 and S_8 yields $[Rh_2L(O_2)_2Cl_2]$ and $[Rh_2L(S_2)_2Cl_2]$, respectively, in which O_2 and S_2 are π-bonded to rhodium. The complex $[Rh_2L(O)_2Cl_2]$ in solution is slowly oxidised to $[Rh_2L(O)_4\ Cl_2]$. All complexes have been characterized and geometric aspects discussed on the basis of ^{31}p-{^{1}H}NMR data.

Keywords: polyhospine; rhodium; synthesis; oxidative addition

INTRODUCTION

Complexes of tertiary phosphine ligands with transition metals of low oxidation state have been used in many important chemical reactions such as oxidative additions,[1] stabilization and activation of small molecules by coordination[2] and

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in the field of homogeneous catalysis.[3] The growing importance of this type of complex, specially rhodium(I) and iridium(I) complexes of chelated tertiary phosphines, is evident from many recent reports in the fields, of structural studies,[4] activation of σ-bonds[5] and catalytic hydrogenation[6] and hydroformylation reactions.[7] Recently a dinuclear rhodium(I) complex of a tertiary phosphine ligand which shows high catalytic activity and regioselectivity in the hydroformylation of olefins has been reported.[7] Over the past few years we have been involved in the chemistry of transition metal complexes of chelated tertiary phospine or arsine ligands.[8] These have some advantages over monodentate phosphines; due to the chelate effect the tendency of phosphino group(s) to be dissociated is minimized during a chemical reaction. There is more control on the stereochemistry of the complexes and due to the presence of σ-donor (N) and π-acceptor (P) coordinating atoms it is possible to control electron density on metal ions, as is important in homogeneous catalysis. We report here the synthesis of a series of dinuclear rhodium(I) complexes of a hexadentate ligand with N_2P_4 donors, *N,N,N′,N′-tetrakis* [2 (diphenylphosphino) ethyl]ethane-1,2-diamine (L) and their reactions with a number of small molecules.

Experimental

Physical Measurements

C, H and N analyses were performed on a model 1106 Carlo Erba Elemental Analyser. Infrared spectra were recorded on a Carl Zeiss Specord M80 spectrophotometer, in KBr pellets. NMR spectra were recorded on a JEOL FX-100 FT instrument. For ^{31}P-{^{1}H} NMR spectra 10 mm tubes with a capillary of deuterium oxide for the internal lock were used.

Materials

Rhodium trichloride hydrate was obtained from Arora-Matthey; 1,5-cyclooctadiene (cod), silver perchlorate and nitrosonium tetrafluoroborate were purchased from Aldrich. Methyl iodide, potassium iodide, potassium bromide and sodium azide were obtained from National Chemicals. Chlorine, carbon monoxide and sulphurdioxide were prepared by laboratory procedures.[9] The ligand (L) was prepared as already described.[8] $[Rh(cod)Cl]_2$ was prepared by a published procedure.[10]

All organic solvents were purified and dried by standard methods before use. All preparations were carried out under dry argon or nitrogen. Solvents used for precipitation of compounds were deaereated. Some filtrations were also carried out under dry argon.

Synthesis of Metal Complexes $[Rh_2LCl_2]$ *1*

To a boiling solution of [Rh(cod) Cl_2 (0.5 mmol) in THF (25 cm^3) L (0.5 mmol) dissolved in deareated THF (10 cm^3) was added dropwise through a pressure equaliser and refluxing continued. After 5h the solution was allowed to cool to room temperature and the product thus deposited was separated by filtration under nitrogen, washed with THF and dried under vacuum; yield 65%. Found: C, 58.29; H, 5.00; N, 2.18%. Calc. for $C_{58}H_{60}Cl_2Rh_2N_2P_4$: C, 58.75; H, 5.10; N, 2.36%.

$[Rh_2LI_2]$ *2 and* $[Rh_2L(N_3)_2]$ *3*

A mixture of [Rh(cod)Cl_2 (0.5 mmol) and KI (in the case of **2**) or NaN_3 (in the case of **3**) (1 mmol) was refluxed for 1h in THF (15 cm^3) - MeOH (15 cm^3) mixture. The solvent was then removed under vacuum and the residue extracted with dichloromethane, filtered and the solvent removed again under vacuum. The residue thus obtained was dissolved in THF and reacted with L (0.5 mmol) following the same procedure as described for **1**; yield 72% (**2**) and 60% (**3**). Found for **2**: C, 50.64; H, 4.58; N, 1.93%; Calc for $C_{58}H_{60}I_2Rh_2N_2P_4$: C, 50.90; H, 4.42; N, 2.05%. Found for **3**: C, 57.84; H, 4.96; N, 9.21%. Calc. for $C_{58}H_{60}Rh_2N_8P_4$: C, 58.11; H, 5.04; N, 9.35%.

$[Rh_2L][ClO_4]_2$ *4*

$AgClO_4$ (1 mmol) was added to $[Rh(cod)Cl]_2$ (0.5 mmol) dissolved in THF (20 cm^3) and the reaction mixture was stirred at 50°C for lh. The white precipitate (AgCl) which separated during stirring was removed by filtration and the filtrate was added dropwise to a boiling solution of L (0.5 mmol) in THF (10 cm^3) and reflux continued for 2h. The reddish-brown compound which deposited during reflux was isolated by filtration, washed with THF and dried under vacuum; yield 75%. Found: C, 52.79; H, 4.64; N, 2.09%. Calc. for $C_{58}H_{60}Cl_2Rh_2N_2O_8P_4$: C, 53.03; H, 4.60; N, 2.13%.

$[Rh_2L(CO)_4]I_2$ *5*

A mixture of $[Rh(cod)Cl]_2$ (0.5 mmol) and KI (2 mmol) in methanol (20 cm^3) and dichloromethane (5 cm^3) was refluxed for 2h and then allowed to cool to room temperature, filtered, and bubbled with CO. After 2h L (0.5 mmol) dissolved in dichloromethane (10 cm^3) was added slowly with stirring at room temperature and bubbling of CO continued for 5h during which a brown compound separated from the reaction mixture. The compound thus obtained was isolated by filtration, washed with dichloromethane and dried under vacuum, yield 60%. Found: C, 50.18; H, 3.96; N, 1.72%, Calc. for $C_{62}H_{60}I_2Rh_2N_2O_4P_4$: C, 50.29; H, 4.08; N, 1.89%.

[Rh_2LCl_6] *6*

Through a solution of [Rh_2LCl_2] (0.2 mmol) in dichloromethane (10 cm^3) chlorine gas was bubbled for 1h at room temperature during which a brown precipitate deposited. Precipitation was completed by adding *n*-hexane (20 cm^3) to the reaction mixture. The compound thus obtained was isolated by filtration and dried under vacuum; yield 90%. Found: C, 52.32; H, 4.62; N, 2.06%. Calc. for $C_{58}H_{60}Cl_6Rh_2N_2P_4$: C, 52.47; H, 4.55; N, 2.11%.

[Rh_2LBr_6] *7*

To a solution of [Rh_2LCl_2] (0.2 mmol) in dichloromethane (10 cm^3) KBr (1 mmol) in methanol (5 cm^3) and bromine (0.2 cm^3) was added at room temperature and stirring continued for 1h. A brown compound which separated was isolated by filtration, washed with a little water, methanol and dichloromethane and dried under vacuum, yield 85%. Found: C, 43.57; H, 3.64; N, 1.64%. Calc. for $C_{58}H_{60}Br_6Rh_2N_2P_4$: C, 43.70; H, 3.79; N, 1.76%.

[Rh_2LI_6] *8*

This compound was prepared following the same procedure as described for **7** except that KI and I_2 were added instead of KBr and Br_2, respectively; yield 90% Found: C, 36.85; H, 3.13; N, 1.38%. Calc. for $C_{58}H_{60}I_6Rh_2N_2P_4$: C, 37.13; H, 3.22; N, 1.49%.

[$Rh_2L(CH_3)_2Cl_2I_2$] *9*

To a solution of [Rh_2LCl_2] (0.2 mmol) in dichloromethane (10 cm^3) CH_3I (0.5 cm^3) was added and the solution stirred in the dark for 0.5 h. A dark brown compound that deposited was isolated by filtration washed with benzene and diethylether and dried under vacuum; yield 80%. Found: C, 48.74; H, 4.58; N, 1.78%. Calc. for $C_{60}H_{66}Cl_2I_2Rh_2N_2P_4$: C, 49.04; H, 4.53; N, 1.91%.

[$Rh_2L(NO)_2Cl_2$] [BF_4]$_2$ *10*

This compound was prepared following the same procedure as described for **9** except that a methanolic solution (5 cm^3) of $NOBF_4$ (1:2 mol ratio) was added instead of CH_3I; yield 70%. Found: C, 48.82; H, 4.20; N, 3.82%. Calc. for $C_{58}H_{60}F_8Cl_2Rh_2B_2N_4O_2P_4$: C, 49.08; H, 4.26; N, 3.95%.

[$Rh_2L(CO)_2Cl_2$] 11 and [$Rh_2L(CO)_2(N_3)_2$] 12

Through a solution of [Rh_2LCl_2] or [$Rh_2L(N_3)_2$] (0.2 mmol) in dichloromethane (50 cm^3) CO was bubbled for 4h. The volume of the solution thus obtained was reduced to *ca* 10 cm^3 under vacuum and *n*-hexane (20 cm^3) added. The orange compound which precipitated was isolated by filtration, washed with *n*-hexane and dried; yield 75–80%. Found for **11**: C, 57.84; H, 4.96; N, 2.16%. Calc. for $C_{60}H_{60}Cl_2Rh_2N_2O_2P_4$: C, 58.03; H, 4.87; N, 2.25%. Found for **12**: C, 57.62; H, 4.68; N, 8.72%. Calc. for $C_{60}H_{60}Rh_2N_8O_2P_4$: C, 57.43; H, 4.82; N, 8.93%.

[$Rh_2L(O)_4(CO_3)_2X_2$] X = Cl (13), I (14) and N_3 (15)

Through a solution of **5**, **11** or **12** (0.2 mmol) in acetonitrile (25 cm^3) O_2 was bubbled for 4h and the solution kept at room temperature. After two days, solvent was removed by rotary evaporator and the residue recrystallized from acetonitrile - benzene (1:1) mixture; yield; 70–80%. Found for **13**: C, 52.28; H, 4.60; N, 1.89%. Calc. for $C_{60}H_{60}Cl_2Rh_2N_2O_{10}P_4$: C, 52.61; H, 4.41; N, 2.04%. Found for **14**: C, 46.14; H, 3.96; N, 1.75%. Calc. for $C_{60}H_{60}I_2Rh_2N_2O_{10}P_4$: C, 46.41; H, 3.89; N, 1.80. Found for **15**: C, 51.78; H, 4.52; N, 8.02%. Calc. for $C_{60}H_{60}Rh_2N_8O_{10}P_4$: C, 52.11; H, 4.37; N, 8.10%.

[$Rh_2L(SO_2)_2Cl_2$] 16

This compound was prepared following the same procedure as described for **11** and **12** except that SO_2 was bubbled for 2h instead of CO; yield 80%. Found: C, 53.26; H, 4.43; N, 1.98%. Calc. for $C_{58}H_{60}Cl_2Rh_2N_2O_4S_2P_4$: C, 53.02; H, 4.60; N, 2.13%.

[$Rh_2L(O)_4(SO_4)_2Cl_2$] 17

Through a dichloromethane solution (50 cm^3) of [Rh_2LCl_2] SO_2 was bubbled for 2h followed by O_2 for another 2h and the solution kept at room temperature for 24h. The compound was then isolated following the same procedure as for **11** and **12**; yield 68%. Found: C, 47.91; H, 4.32%; N, 1.87%. Calc. for $C_{58}H_{60}Cl_2Rh_2N_2O_{12}S_2P_4$: C, 48.31; H, 4.19; N, 1.94%.

[$Rh_2L(O_2)_2Cl_2$] · CH_2Cl_2 18

Through a solution of [Rh_2LCl_2] (0.2 mmol) in dichloromethane O_2 was bubbled for 2h. The solvent was then removed by flushing O_2 through the solution and the compound dried under vacuum. Found: C, 52.63; H, 4.36; N, 1.91%. Calc. for $C_{59}H_{62}Cl_4Rh_2N_2O_4P_4$: C, 53.09; H, 4.68; N, 2.10%.

[$Rh_2L(O)_4Cl_2$] 19

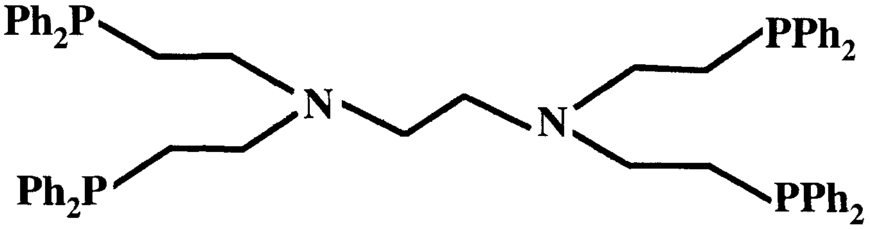
Through a dichloromethane solution of [Rh_2LCl_2] O_2 was bubbled for 2h and the solution kept at room temperature for 24h. The volume of solution was then reduced to *ca* 5 cm^3 and on adding *n*-hexane (25 cm^3) an orange compound precipitated, yield 85%. Found: C, 55.47; H, 4.96; N, 2.18%. Calc. for $C_{58}H_{60}Cl_2Rh_2N_2O_4P_4$: C, 55.74; H, 4.84; N, 2.24%.

[$Rh_2L(S_2)_2Cl_2$] 20

Sulfur (S_8 1 mmol) dissolved in benzene (5 cm^3) was added dropwise to [Rh_2LCl_2] (0.2 mmol) dissolved in dichloromethane (5 cm^3) and stirring continued for 1h. A dark brown compound that separated was isolated by filtration, washed with benzene and diethylether and dried; yield 75%. Found: C, 52.69; H, 4.59; N, 2.00%. Calc. for $C_{58}H_{60}Cl_2Rh_2N_2P_4S_4$: C, 53.02; H, 4.60; N, 2.13%.

Results and Discussion

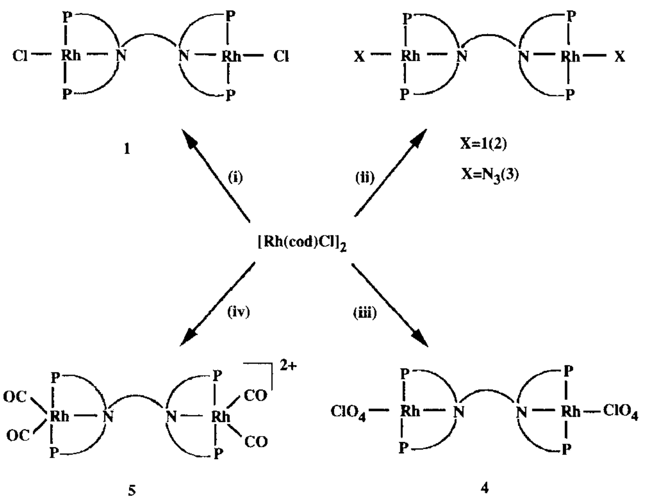
Reaction of the dimeric compound [Rh(cod)Cl]$_2$ with L in THF resulted in the formation of a dinuclear complex [Rh_2LCl_2] **1** with good yield. Reaction of [Rh(cod)Cl_2 with KI or NaN_3 followed by with L under similar conditions yielded [Rh_2LI_2] **2** and [$Rh_2L(N_3)_2$] **3**, respectively. These complexes are stable in the solid state in an inert atmosphere but in the presence of air they change slowly in solid state and rapidly in solution. IR spectra of **3** show a strong band at 2045 cm^{-1} due to υ asym (N_3) of coordinated azide.[11] ^{31}P-{^1H} NMR spectra of **1** exhibits a doublet at δ 32.15 (Table I) with a coupling constant of 87.9 Hz. L, however, shows a singlet at δ −19.01. ^{31}P-{^1H} NMR data for **1**, therefore, indicate all four phosphorus atoms of PPh_2 are equivalent and coordinated to rhodium. The appearance of a doublet is due to coupling of phosphorus with the ^{103}Rh nucleus having $S = 1/2$. The δ value[8b, 12, 13] and coupling constant[5b, 13] are in the range found for similar systems with square planar geometry having phosphorus atoms *trans* to each other. Data of **1**, therefore, suggest a dinuclear complex with square planar geometry about rhodium having phosphorus atoms in *trans* positions, as shown in Scheme 1. ^{31}P-{^1H} NMR spectra of **3** also exhibit a doublet at δ 32.18 with $J_{Rh\text{-}P} = 80.6$ Hz, which indicates a similar geometry to **1**. ^{31}P-{^1H} NMR spectra of **2** were not recorded due to its high air sensitivity and poor solubility but, by analogy, a similar geometry may be assigned. Reaction of [Rh(cod)Cl_2 with $AgClO_4$ and then with L resulted in the formation of [Rh_2L] [ClO_4]$_2$ **4**. IR spectra of **4** show a strong broad band centred at 1100 cm^{-1} and a sharp band at 620 cm^{-1} which may be assigned to (ClO_4).[14] ^{31}P-{^1H} NMR of (**4**) in acetonitrile exhibits a doublet at 39.50 with $J_{Rh\text{-}P}$ = 119.6 Hz, which indicates all phosphorus atoms are equivalent. The data suggest a binuclear complex with similar geometry for both rhodium atoms in acetonitrile solution, the solvent is involved in coordination instead of a weak coordinating group like ClO_4^- as indicated by conductivity measurements in same solvent (Λ_M = 234 Ω^{-1} cm^2 mol^{-1}) and equipments to a square planar geometry for rhodium. As the compound was prepared in THF which has very weak coordinating ability and there is no indication of its involvement in coordination, in the solid state ClO_4^- may be weakly coordinated to rhodium. A small low field shift of the $^{31}P\text{-}\{^1H\}$ NMR resonance as compared to that of **1** and **3** may be due to its cationic nature. Reaction of $[Rh(cod)Cl_2$ with KI followed by bubbling of CO in dichloromethane and subsequent reaction with L resulted in the formation of a complex of composition $[Rh_2L(CO)_4]I_2$ **5**. The compound behaves as a 1:2 electrolyte in DMF (Λ_M =138 Ω^{-1} cm^2 mol^{-1}). IR spectra of **5** show a strong band at 2020 cm^{-1} which may be assigned to υ (CO).[1b, 15] This indicates there is only one type of IR-active CO group in **5**. The $^{31}P\text{-}\{^1H\}$ NMR spectra exhibit a doublet at δ 44.77 with $J_{Ph\text{-}P}$ = 134.3 Hz, which indicates that all phosphorus atoms in **5** are equivalent and coordinated to rhodium. The value also indicates that the coordinated phosphorus atoms are not *trans* to CO. On the basis of these data a trigonal bipyramidal geometry having two phosphorus atoms with nitrogen in the trigonal plane and CO in axial positions or two CO groups with nitrogen in the trigonal plane and phosphorus atoms in axial positions is possible. The first requires a N—Rh—P bond angle of about 120°; such a situation with a —CH_2—CH_2— linkage between nitrogen and phosphorus atoms provides strong strain on the N—P linkage. Therefore, the latter possibility as shown in Scheme 1 is assigned for **5**. A small low field shift of the $^{31}P\text{-}\{^1H\}$ NMR signal compared to complexes **1** and **3** is due to the cationic nature of **5**.



(L)

TABLE I ^{31}P—{^{1}H} NMR data for the rhodium complexes

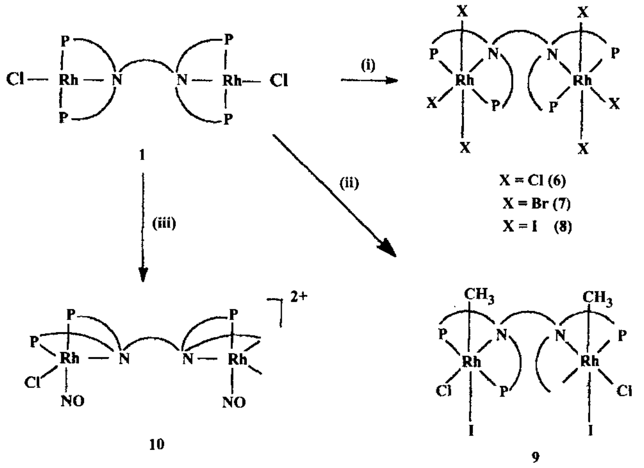
Compound		*Solvent*	δ	$J_{Rh—P}$
	L	$CHCl_3$	−19.01	
1	$[Rh_2LCl_2$	$CHCl_3$	32.15	87.9
3	$[Rh_2L(N_3)_2]$	DMF	32.18	80.6
4	$[Rh_2L][ClO_4]_2$	CH_3CN	39.50	119.6
5	$[Rh_2L(CO)_4I_2]$	DMF	44.77	134.3
6	$[Rh_2LCl_6]$	DMF	35.36	117.2
7	$[Rh_2LBr_6]$	DMF	35.96	139.2
9	$[Rh_2L(CH_3)_2Cl_2I_2]$	DMF	38.45	130.7
10	$[Rh_2L(NO)_2Cl_2][BF_4]_2$	DMF	15.17[a]	105.0
			33.06[a]	112.3
11	$[Rh_2L(CO)_2Cl_2]$	CH_2Cl_2	33.48	92.8
13	$[Rh_2L(O)_4(CO_3)_2Cl_2]$	DMF	30.82	
14	$[Rh_2L(O)_4(CO_3)_2I_2]$	DMF	30.90	
15	$[Rh_2L(O)_4(CO_3)_2(N_3)_2]$	DMF	30.60	
17	$[Rh_2L(O)_4(SO_4)_2Cl_2]$	DMF	31.97	
19	$[Rh_2L(O)_4Cl_2]$	$CHCl_3$	29.79	



SCHEME 1 (i)L; (ii) NaI or NaN_3, L; (iii) $AgClO_4$, L; (iv) NaI, CO, L.

Reactions of 1 with Cl_2, Br_2, I_2, MeI and $NOBF_4$

The square planar dinuclear complex $[Rh_2LCl_2]$ **1** readily undergoes oxidative addition. Reaction of a dichloromethane solution of **1** with Cl_2 or Br_2 in presence of KBr, or I_2 in presence of KI, MeI and $NOBF_4$ resulted in the formation of $[Rh_2LX_6]$ (X = Cl **6**, Br (**7**) and I (**8**)), $[Rh_2L(Me)_2Cl_2I_2]$ (**9**) and $[Rh_2L(NO)_2Cl_2][BF_4]_2$ (**10**). The complexes **6** – **10** are less soluble in dichloromethane as compared to the parent compound and precipitated during reaction except for complex **6** which was partially precipitated during reaction and completely on addition of *n*-hexane. IR spectra of complexes **6** – **9** show no significant change compared to the parent complex. Complex **10** exhibits a strong band at 1670 cm^{-1} which is in the range usually cited for a bent M—N—O linkage[1c,26] and a strong broad band centred at 1060 cm^{-1} which can be assigned to BF_4^-.[18] ^{1}H NMR spectra of **9** in DMSO-d_6 exhibit a broad peak at δ 1.23 which may be assigned to Rh-C*H*$_3$.[5b,19] ^{31}-{^{1}H} NMR data (Table I) for **6**, **7** and **9** in DMF are similar to those of **1** except for a slight low field shift of the phosphorus signal and an increase in $J_{Rh\text{-}P}$ values. On the basis of these data an octahedral geometry of rhodium with the added species in axial positions is suggested, as shown in Scheme 2. The ^{31}P-{^{1}H} NMR spectra of **10** shows two doublets of doublets at δ 15.17 and 33.48 with $J_{P\text{-}P}$ values of 12.2 Hz and $J_{Rh\text{-}P}$ values of 105.0 and 112.3 Hz, respectively. The $J_{P\text{-}P}$ value indicates that the two non-equivalent phosphorus atoms are in *cis* positions.[13, 17, 20] On the basis of these data a TBP geometry for rhodium with *cis* phosphorus atoms is assigned. The signal at σ15.17 is assigned to a phosphorus atom *trans* to NO.[8j]

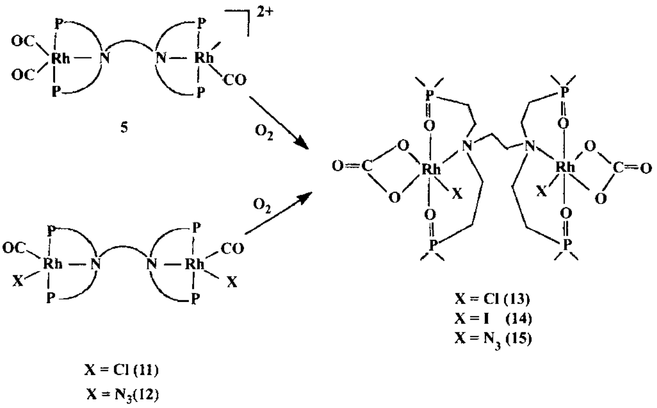


SCHEME 2 (i) Cl_2; KBr, Br_2; KI, I_2; (ii) CH_3I; (iii) $NOBF_4$.

Reactions with CO

Reactions of [Rh_2LCl_2] (**1**) and [$Rh_2L(N_3)_2$] (**3**) with CO in dichloromethane resulted in the formation of [$Rh_2L(CO)_2Cl_2$] (**11**) and [$Rh_2L(CO)_2(N_3)_2$] (**12**), respectively. These complexes are air-sensitive in solution. IR spectra of **11** and **12** exhibit a strong band at 1990 and 1995 cm^{-1}, respectively, which may be assigned to υ(CO); [1b, 15] in addition, **12** shows a strong band at 2058 cm^{-1} which is assigned to coordinated $\delta_{asym}(N_3)$.[11] ^{31}P-{^{1}H} NMR spectra of **11** show a doublet at δ 33.48 with

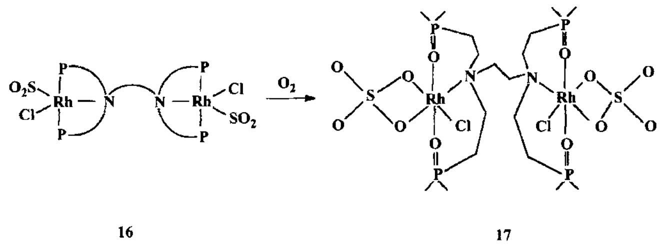
$J_{Rh\text{-}P}$ = 92.8 Hz. Data are consistent with a TBP geometry for rhodium with phosphorus atoms in axial positions, as shown in Scheme 3. Complex **12** is expected to have similar geometry. All CO adducts, **5, 11** and **12** react with O_2 in acetronitrile and the end products isolated are $[Rh_2L(O)_4(CO_3)_2X_2]$, X = Cl (**13**), I (**14**) and N_3 (**15**). IR spectra of **13 - 15** exhibit no CO bands but new strong bands at 1665, 1612, 1170 and 1125 cm^{-1} appear. The first two indicate the formation of bidentate carbonate as found in other systems.[15, 2e, 21] The absorptions at 1170 and 1125 cm^{-1} are due to phosphine oxide.[1b–1c, 2c, 22] $^{31}P\text{-}\{^1H\}$ NMR spectra of all three complexes, **13 – 15**, in DMF give a singlet at δ 30.7 ± 0.1 which is close to that of triphenylphosphine oxide. IR and ^{31}P NMR data therefore suggest the formation of phosphine oxides which are bound to the metal through oxygen.[22, 23] Long range coupling of rhodium-phosphine [24] could not observed at room temperature; data, therefore, suggest an octahedral geometry of rhodium with phosphine oxide in axial positions, as shown in Scheme 3.



SCHEME 3

Reaction with SO_2

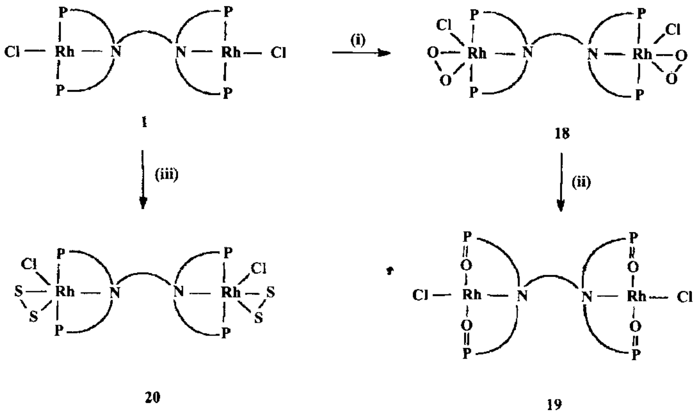
When SO_2 is bubbled through a dichloromethane solution of $[Rh_2LCl_2]$ (**1**) a compound of composition $[Rh_2L(SO_2)_2Cl_2]$ (**16**) formed. Coordination of SO_2 through sulfur was indicated by IR spectra which show new bands at 1148 and 1050 cm^{-1}.[1a, 1c, 2b, 21] $^{31}P\text{-}\{^1H\}$ NMR spectra of the compound could not be recorded as the freshly prepared solution of the isolated complex was not sufficiently stable and it reacts with O_2. The SO_2 adduct (**16**) was isolated from SO_2-saturated solution. By comparison with pentacoordinate CO adducts (**11** and **12**) TBP geometry for rhodium in **16** may be assigned as shown in Scheme 4. A dichloromethane solution of $[Rh_2LCl_2]$ on reaction with SO_2 for 2h followed by with O_2 for another 2h gave $[Rh_2L(O)_4(SO_4)_2Cl_2]$ (**17**). IR spectra of **17** show strong bands at 1252, 1145, 1055 and a weak band at 640 cm^{-1} which can be assigned to bidentate SO_4^{2-},[1a–c, 21] two strong bands at 1170 and 1130 cm^{-1} are due to phosphine oxide. ^{31}P-{^1H} NMR spectra of **17** in DMF exhibit a singlet at δ 31.97, similar to that in **13** – **15**. On the basis of these data and comparison with **13** – **15**, octahedral geometry is suggested for **17**, as shown in Scheme 4.



SCHEME 4

Reactions with O_2 and S_8

The complex **1** reacts with O_2 to give the product, $[Rh_2L(O_2)_2Cl_2]$ (**18**), which has a strong IR band at 840 cm^{-1}. The experiment was repeated with the azido complex (**3**) and the same IR band was obtained. When the solution was kept over night, the isolated compound, $[Rh_2L(O)_4Cl_2]$ (**19**), shows no IR band at 840 cm^{-1} but strong bands at 1175 and 1125 cm^{-1}. The IR band at 840 cm^{-1} is in the range usually assigned to the RhO_2 mode[1a,1c] and the latter in **19** are due to phosphine oxide. ^{31}P-{^1H} NMR spectra of **19** (δ 29.79) are similar to those of **13** – **15** which indicates the formation of phosphine oxide. The observation, therefore, indicates that complex **1** with O_2



SCHEME 5 (i) O_2; (ii) 24 h in solution; (iii) S.

forms a rhodium-dioxygen adduct which slowly transfers oxygen to coordinated PPh_2 of phosphine oxide to give $Ph_2P{=}O$ attached to rhodium through oxygen. The new compound thus formed shows no tendency to interact further with O_2 to form any dioxygen adduct. The probable geometrics of **18** and **19** are shown in Scheme 5.

A disulphur complex, $[Rh_2L(S_2)_2Cl_2]$ (**20**), was prepared by adding a benzene solution of sulphur to a dichloromethane solution of $[Rh_2LCl_2]$ (**1**) at room temperature. Compound **20** was precipitated during reaction and the solid product shows an IR band of medium intensity at 542 cm^{-1}, assigned to a π-bonded disulphur group (RhS_2)[1c, 25, 26] geometry similar to that of the analogous dioxygen complex is assigned. When O_2 was bubbled through a solution of **20** the isolated crude product shows IR bands due to phosphine oxide and SO but a pure compound could not be isolated. In oxygen-free solution the compound also changes slowly and the IR shows a weak band at 580 cm^{-1}, which may be due to the formation of $Ph_2P{=}S$[25, 27] but the product could not be isolated in pure form.

References

[1] (a) J. Valentine, D. Valentine Jr. and J.P. Collman, *Inorg. Chem.*, **10**, 219 (1971); (b) W.O. Siegl, S.J. Lapporte and J.P. Collman, *Inorg. Chem.*, **10**, 2158 (1971); (c) T.E. Nappier Jr., D.W. Meek, R.M. Kirchner and J.A. Ibers, *J. Am. Chem. Soc.* **95**, 4194 (1973); (d) C. Bianchini, A. Meli, M. Peruzzini, F. Vizza and P. Frediani, *Organometallics*, **9**, 1146 (1990); (e) C. Bianchlini, C.J. Elsevier, J.M. Ernsting, M. Peruzzini and F. Zanobini, *Inorg. Chem.*, **34**, 84 (1995).

[2] (a) T.E. Nappier Jr. and D.W. Meek, *J. Am. Chem. Soc.*, **94**, 306 (1972); (b) D.C. Moody and R.R. Ryan, *J. Chem. Soc., Chem. Commun.*, 503 (1976); (c) C. Bianchini, C. Mealli, A. Meli and M. Sabat, *Inorg. Chem.*, **23**, 2731 (1984); (d) C. Bianchini, C. Mealli, A. Meli and M. Sabat, *J. Chem. Soc., Chem. Commun.*, 1024 (1985); (e) C. Bianchini, C. Mealli, M. Peruzzini and F. Zanobini, *J. Am. Chem. Soc.*, **109**, 5548 (1987).

[3] (a) D.W. Meek, *Homogeneous Catalysis with metal phosphine complexes*, (Plenum Press, New York, 1983); (b) B.T. Heaton, J.A. Iggo, C. Jacob, J. Nadarajah, M.A. Fontaine, R. Messere and A.F. Noels, *J. Chem. Soc., Dalton Trans*; 2875 (1974); (c) M.C. Simpson, M.J. Payne and D.J. Cole-Hamilton, *J. Chem. Soc., Dalton Trans*; 2899 (1994).

[4] (a) S.A. Laneman, F.R. Fronczek and G.G. Stanley, *J. Am. Chem. Soc.*, **110**, 5585 (1988); (b) F.A. Cotton and B. Hong, *Prog. Inorg. Chem.*, **40**, 179 (1992); (c) S.A. Westcott, G. Stringer, S. Anderson, N.J. Taylor and T.B. Marder, *Inorg. Chem.*, **33**, 4589 (1994); (d) D.M. Heinekey, A. Liegeois and M. Van Room, *J. Am. Chem. Soc.*, **116**, 8388 (1994).

[5] (a) C. Bianchini, A. Meli, M. Peruzzini, F. Vizza and F. Zanobini, *Coord. Chem. Rev.*, **120** 193 (1992); (b) C. Bianchini, D. Masi, A. Meli, M. Peruzzini and F. Zanobini, *J. Am. Chem. Soc.*, **110**, 6411 (1988); (c) C. Bianchini, P. Barbaro, A. Meli, M. Peruzzini, A. Vacca and F. Vizza, *Organometallics*, **12**, 2505 (1993); (d) C. Bianchini, P. Frediani, V. Herrera, M.V. Jimenez, A. Meli, L. Rincon, R.S. Delgado and F. Vizza, *J. Am. Chem. Soc.*, **117**, 4333 (1995).

[6] (a) C. Bianchini, E. Farnetti, M. Graziani, J. Kaspar and F. Vizza, *J. Am. Chem. Soc.*, **115**, 1753 (1993); (b) G.E. Ball, W.R. Cullen, M.D. Fryzuk, W.J. Henderson, B.R. James and K.S. MacFarlane, *Inorg. Chem.*, **33**, 1464 (1994); (c) C. Bianchini, A. Meli, M. Peruzzini, F. Vizza, S. Moneti, V. Herrera and R.A. Sanchez-Delgado, *J. Am. Chem. Soc.*, **116**, 4370 (1994).

[7] (a) G. Suss-Fink, *Angew. Chem. Int. Ed. Eng.*, **33**, 67 (1994); (b) M.E. Broussard, B. Juma, S.G. Train, W.J. Peng, S.A. Laneman and G.G. Stanley, *Science*, **260**, 1784 (1993).

[8] (a) M.M. Taqui Khan, H.C. Bajaj, M.R.H. Siddiqui, B.T. Khan, M.S. Reddy and K.V. Reddy, *J. Chem. Soc., Dalton Trans.*, 2603 (1985); (b) M.M. Taqui Khan and V.V.S. Reddy, *Inorg. Chem.*, **25**, 208 (1986); (c) M.M. Taqui Khan and B. Swami, *Inorg. Chem.*, **26**, 178 (1987); (d) M.M. Taqui Khan, P. Paul, K. Venkatasubramanian and S. Purohit, *J. Chem. Soc. Dalton Trans*, 3405 (1991); (e) M.M. Taqui Khan, P. Paul, K. Venkatasubramanian and S. Purohit, *Inorg. Chim. Acta*, **183**, 229 (1991); (f) M.M. Taqui Khan, P. Paul and K. Venkatasubramanian, *Polyhedron*, **10**, 1827 (1991); (g) M.M. Taqui Khan, P. Paul and S. Purihit, *Inorg. Chim. Acta*, **189**, 165 (1991); (h) P. Paul and K. Venkatasubramanian, *Polyhderon*, **12**, 835 (1993); (i) P. Paul, K. Venkatasubramanian and S. Purohit, *J. Coord. Chem.* **28**, 279 (1993); (j) P. Paul, *Polyhedron*, **12**, 2057 (1993); (k) P. Paul and B. Tyagi, *Polyhedron*, **15**, 675 (1996).

[9] *Mellor's Modern Inorganic Chemistry*, Ed., G.D. Parkes, (*Longmans*, London, 1956).

[10] J. Chatt and L.M. Venanzi, *J. Chem. Soc. A.*, 4735 (1957).

[11] P. Paul and K. Nag, *Inorg. Chem.*, **26**, 2969 (1987).

[12] M.M. Taqui Khan, V.V.S. Reddy and H.C. Bajaj, *Polyhedron*, **6**, 921 (1987).

[13] M.M. Taqui Khan and E. Rama Rao, *Polyhedron*, **6**, 1727 (1987).

[14] P. Paul and K. Nag, *Inorg. Chem.*, **26**, 1586 (1987).

[15] C. Fyhr and M. Garland, *Organometallics*, **12**, 1753 (1993).

[16] M.M. Taqui Khan and A.P. Reddy, *Polyhedron*, **6**, 2009 (1987).

[17] J.B. Letts, T.J. Mazanec and D.W. Meek, *J. Am. Chem. Soc.*, **104**, 3898 (1982).

[18] D.L. DuBois and A. Miedaner, *Inorg. Chem.*, **25**, 4642 (1986).

[19] J.A. Tiethof, J.L. Peterson and D.W. Meek, *Inorg. Chem.*, **15**, 1365 (1976).

[20] M.M. Taqui Khan and E. Rama Rao, *Polyhedron*, **7**, 29 (1988).

[21] B.L. Booth, C.A. McAuliffe and G.L. Stanley, *J. Organomet. Chem.*, **226**, 191 (1982).

[22] F.A. Cotton, R.D. Barnes and E. Bannister, *J. Chem. Soc.*, 2199 (1960).

[23] S.M. Godfrey, D.G. Kelly, C.A. McAuliffe and R.G. Pritchard, *J. Chem. Soc., Dalton Trans*, 1095 (1995).

[24] C. Bianchini, A. Meli, M. Peruzzini and F. Zanobini, C. Bruneau and P.H. Dixneuf, *Organometallics*, **9**, 1155 (1990).

[25] A.P. Ginsberg and W.F. Lindsell, *J. Chem. Soc., Chem. Commun.* 232 (1971).

[26] W.D. Bonds Jr. and J.A. Ibers, *J. Am. Chem. Soc.*, **94**, 3413 (1972).

[27] P. Nicpon and D.W. Meek, *Inorg. Chem.* **6**, 145 (1967).