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Transition metal chemistry of phosphorus based ligands: synthesis and transition metal chemistry of *N*,*N*′-dimethyl,-bis(diphenylphosphino)ethylenediamine. The crystal and molecular structure of [ReBr(CO)$_3${Ph$_2$PN(Me)CH$_2$CH$_2$(Me)NPPh$_2$}]

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Abstract

The bis(phosphine), Ph$_2$PN(CH$_3$)CH$_2$CH$_2$N(CH$_3$)PPh$_2$ reacts with Group 6 metal carbonyl derivatives, [ReBr(CO)$_3$(NCMe)$_2$] and [MCl$_2$(COD)] (M = Pd or Pt) to give the corresponding seven-membered chelate complexes. The compounds have been characterized by elemental analysis, IR and NMR spectroscopic data. The structure of the rhenium complex, [ReBr(CO)$_3${Ph$_2$PN(CH$_3$)CH$_2$CH$_2$(CH$_3$)NPPh$_2$}] has been confirmed by X-ray crystallography. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Bis(phosphines); Ethylenediamine derivatives; Transition metal complexes; Mononuclear; Chelate complexes

1. Introduction

The interest in synthesis and transition metal chemistry of bis(phosphine) ligands is becoming increasingly important in view of their potential applications in organic synthesis [1–5]. Often organic transformations are carried out by the *in situ* generation of a metal catalyst by reacting a ligand with a suitable metal precursor in solution containing the reagents and the substrates; in such processes the catalytic path cannot be explained properly as there will be a lack of information about the compatibility of the metal reagent and the ligand under those reaction conditions [6,7]. In this context, understanding of the coordination behavior of these ligands with a variety of transition metals is vital as it gives the basic information about the reactivity, the stability and the steric and electronic situation around the metal center. Although bis(phosphines) with varied lengths of the carbon backbone have been extensively studied, the two phosphorus centers separated by more than one type of spacers (atoms or groups) are less extensive. Further the transition metal chemistry of this class of ligand is interesting, owing to the variation in the electronegativity of spacer atoms that greatly influences the donor–acceptor properties of the phosphorus centers. Also, the seven-membered chelate rings are relatively less stable when compared to the five- and six-membered rings; one of the metal–phosphorus bonds can be readily cleaved for further reactions and for catalytic purposes. Many bis(phosphines) derived from the ethylenediamine backbone have been used as catalysts in organic synthesis [6,7]. As a part of our interest [8–13] and for others [14–16] in designing bidentate, tridentate or polydentate phosphorus based ligands having more than one type of heteroatoms or groups in the backbone for complexation studies and catalytic applications, we report here the transition metal chemistry of bis(phosphine), Ph$_2$PN(Me)CH$_2$CH$_2$N(Me)PPh$_2$. The rhenium complex, [ReBr(CO)$_3${Ph$_2$PN(CH$_3$)CH$_2$CH$_2$(CH$_3$)NPPh$_2$}] (**5**) is structurally characterized.

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2. Experimental

2.1. General considerations

All experimental manipulations were performed under the atmosphere of dry nitrogen. Standard Schlenk and vacuum line techniques were used. Solvents were dried and distilled prior to use. The ^{1}H- and ^{31}P-NMR spectra were recorded on a VXR 300 spectrometer operating at the appropriate frequencies using tetramethylsilane and 85% H_3PO_4 as internal and external references, respectively. $CDCl_3$ was used as both solvent and internal lock. Positive shifts lie downfield in all cases. Infrared spectra were recorded in nujol mull or KBr disc. Microanalyses were carried out in the Department of Chemistry, IIT, Bombay.

2.2. Starting compounds

N,*N*′-Dimethylethylenediamine was obtained from Lancaster Synthesis Ltd, and used without purification. $[M(CO)_4(NBD)]$, (M = Cr [17], Mo [18]) $[W(CO)_4(pip)_2]$ [19], $[MCl_2(COD)]$ (M = Pd [20] or Pt [21]) and $[ReBr(CO)_3(NCMe)_2]$ [22] were prepared according to published procedures or with minor changes thereof.

2.3. Preparation of $Ph_2PN(CH_3)CH_2CH_2N(CH_3)PPh_2$ (1)

The above ligand was prepared by modifying the procedure of Mortreux et al. [23] as follows.

A solution of PPh_2Cl (2.18 g, 9.89 mmol) in dry diethyl ether (30 ml) was added with stirring to a solution of *N*,*N*′-dimethylethylenediamine (0.871 g, 9.89 mmol) at −10°C. The stirring was continued for 3 h and the solution was warmed to 0°C and Et_3N (2.1 g, 20.75 mmol) in dry diethyl ether (20 ml) was added followed by the dropwise addition of PPh_2Cl (2.18 g, 9.89 mmol) in a mixture of diethyl ether (25 ml) and hexane (15 ml). Stirring was continued for 24 h at room temperature (r.t.). The reaction mixture was then filtered. The white solid obtained was consecutively washed with water, MeOH and diethyl ether and dried under vacuum. The compound was crystallized from a 1:1 mixture of CH_2Cl_2–hexane. (3.55 g, 78%). m.p. 184–187°C. Anal. Found: C, 73.6; H, 6.6; N, 6.1. Calc. for $C_{28}H_{30}N_2P_2$: C, 73.7; H, 6.6; N, 6.1%. ^{1}H-NMR ($CDCl_3$): δ 6.82–7.41 (m, 20H, phenyl), 3.28 (s, 4H, CH_2CH_2); 2.44 (t, 6H, N-CH_3). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 61.9 (s, 2P).

2.4. Preparation of $[M(CO)_4\{Ph_2PN(CH_3)CH_2CH_2(CH_3)NPPh_2\}]$ (2, M = Cr; 3, M = Mo)

A mixture of **1** (0.117 mmol) and $[M(CO)_4(NBD)]$ (M = Cr or Mo) (0.115 mmol) was heated under reflux in dry hexane (15 ml) for 24 h after which it was filtered hot. The filtrate was then cooled to 0°C to give analytically pure products in good yield.

2. Yield 98%, m.p. 150°C. Anal. Found: C, 61.8; H, 4.8; N, 4.4. Calc. for $C_{32}H_{30}N_2O_4P_2Cr$: C, 61.9; H, 4.8; N, 4.5%. IR (KBr, cm^{-1}): ν(CO) 1874(vs), 1913(br), 2012(vs). ^{1}H-NMR ($CDCl_3$): δ 7.26 (m, 20H, phenyl), 3.46 (dd, 4H, CH_2CH_2), 2.46 (t, 6H, N-CH_3). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 111.1 (s, 2P).

3. Yield 63%, m.p. 129–130°C. Anal. Found: C, 57.8; H, 4.5; N, 4.1. Calc. for $C_{32}H_{30}N_2O_4P_2Mo$: C, 57.8; H, 4.5; N, 4.2%. IR (KBr, cm^{-1}): ν(CO) 1874(vs), 1894(s), 1926(vs), 2019(vs). ^{1}H-NMR ($CDCl_3$): δ 7.26 (m, 20H, phenyl), 3.48 (dd, 4H, CH_2CH_2), 2.48 (t, 6H, N-CH_3). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 91.7 (s, 2P).

2.5. Preparation of $[W(CO)_4\{Ph_2PN(CH_3)CH_2CH_2(CH_3)NPPh_2\}]$ (4)

A mixture of **1** (0.050 g, 0.11 mmol) and $[W(CO)_4(pip)_2]$ (0.050 g, 0.10 mmol) was heated under reflux in dry CH_2Cl_2 (10 ml) for 6 h. The solution was concentrated to about 5–7 ml under reduced pressure and diluted with 2 ml hexane. Cooling to 0°C gives analytically pure product in 67% yield, m.p. 130–132°C. Anal. Found: C, 51.0; H, 3.9; N, 3.6. Calc. for $C_{32}H_{30}N_2O_4P_2W$: C, 51.1; H, 4.0; N, 3.7%. IR (KBr, cm^{-1}): ν(CO) 2010(s) 1952(br), 1986(s). ^{1}H-NMR ($CDCl_3$): δ 7.08 (m, 20H, phenyl), 3.01 (dd, 4H, CH_2CH_2), 2.31 (t, 6H, N-CH_3). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 75.1 (s, 2P), $^1J_{P-W} = 258.6$ Hz.

2.6. Preparation of $[ReBr(CO)_3\{Ph_2PN(CH_3)CH_2CH_2(CH_3)NPPh_2\}]$ (5)

A solution of **1** (0.031 g, 0.06 mmol) in CH_2Cl_2 (7 ml) was added dropwise with stirring to a solution of $[ReBr(CO)_3(NCMe)_2]$ (0.029 g, 0.06 mmol) also in CH_2Cl_2 (7 ml) at r.t. The reaction mixture was allowed to stir for 1 h. The solution was then concentrated to 5 ml under reduced pressure and diluted with 3 ml of hexane and cooled to 0°C to give crystalline product. Yield 86%, m.p. 190–191°C (decomposes). Anal. Found: C, 46.1; H, 3.7; N, 3.4. Calc. for $C_{31}H_{30}BrN_2O_3P_2Re$: C, 46.2; H, 3.7; N, 3.5%. IR (KBr, cm^{-1}): ν(CO) 1913(vs), 1953(vs), 2032(vs). ^{1}H-NMR ($CDCl_3$): δ 7.26 (m, 20H, phenyl), 3.48 (dd, 4H, CH_2CH_2), 2.48 (t, 6H, N-CH_3). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 91.6 (s, 2P).

2.7. Preparation of $[MCl_2\{Ph_2PN(CH_3)CH_2CH_2(CH_3)NPPh_2\}]$ [6, M = Pd; 7, Pt]

A mixture of **1** (0.08 mmol) and $[MCl_2(COD)]$ (M = Pd or Pt) (0.08 mmol) is stirred in CH_2Cl_2 (10 ml) at 25°C for 6 h. The reaction mixture is then concentrated to 5 ml under reduced pressure and 3 ml hexane is added and stored at 0°C for 24 h to give analytically pure products.

6. Yield 52%, m.p. 150–152°C. Anal. Found: C, 53.1; H, 4.7; N, 4.4. Calc. for $C_{28}H_{30}Cl_2N_2P_2Pd$: C, 53.1; H, 4.8; N, 4.4%. ^{1}H-NMR ($CDCl_3$): δ 7.26 (m, 20H, phenyl), 3.38 (dd, 4H, CH_2CH_2), 2.46 (t, 6H, N-CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 79 (s, 2P).

7. Yield 50%, m.p. 180–184°C. Anal. Found: C, 46.4; H, 4.1; N, 3.8. Calc. for $C_{28}H_{30}Cl_2N_2P_2Pt$: C, 46.5; H, 4.2; N, 3.9%. ^{1}H-NMR ($CDCl_3$): δ 7.26 (m, 20H, phenyl), 3.39 (dd, 4H, CH_2CH_2), 2.46 (t, 6H, N-CH_3). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 55.7 (s, 2P). $^1J_{Pt-P} = 4024.5$ Hz.

Table 1
Crystal data for complex $[Re(CO)_3Br\{PPh_2N(Me)CH_2CH_2(Me)NPPh_2\}]$ (**5**)

Empirical formula	$C_{31}H_{30}BrN_2O_3P_2Re$
Formula weight	806.62
Crystal system	Monoclinic
Space group	$P2(1)/n$
Unit cell dimensions	
a (Å)	11.9550(13)
b (Å)	17.6060(16)
c (Å)	14.9030(11)
β (°)	99.459(8)°
V (Å^3)	3094.1(5)
Z	4
D_{calc} (g cm^{-1})	1.732
F (000)	1576
Crystal size (mm)	0.5 × 0.4 × 0.4
Reflections observed	5490
Max 2θ (°)	25.31
R	0.0335
R_w	0.0444
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0335$, $wR_2 = 0.0793$
R indices (all data)	$R_1 = 0.0444$, $wR_2 = 0.0948$
Goodness-of-fit on F^2	1.233

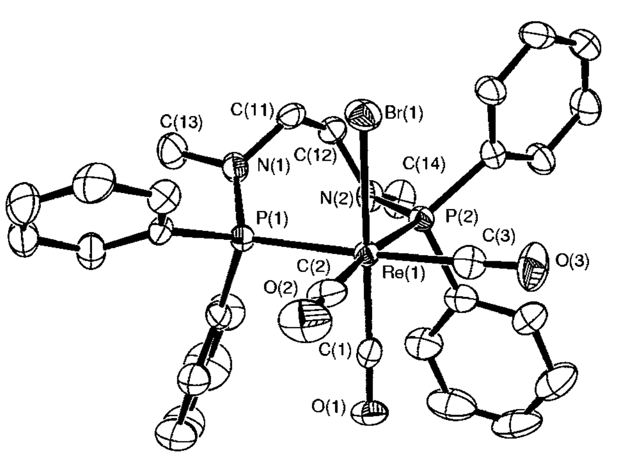


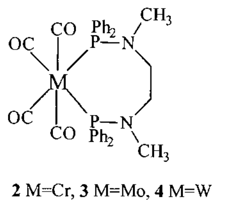
Fig. 1. Perspective ORTEP [26] view of **5** showing the atom numbering scheme. Hydrogen atoms are omitted for clarity.

2.8. Crystal structure determination of $[ReBr(CO)_3\{PPh_2N(Me(CH_2CH_2(Me)NPPh_2\}]$ (5)

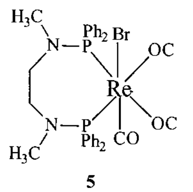
A colorless crystal of **5** (0.5 × 0.4 × 0.4 mm) crystallized from CH_2Cl_2 at 0°C was mounted on a Pyrex filament with epoxy resin. Unit cell dimensions were determined from 25 well centered reflections ($11.5 < \theta < 14.1$). Intensity data were collected (at 293(2) K) with a Nonium MACH3 diffractometer using graphite-monochromated Mo–K$_\alpha$ ($\lambda = 0.71073$ Å) radiation. Parameters are given in Table 1. The structure was solved by direct methods [24] and refined by using SHELXS-97 software [25]. The non-hydrogen atoms were refined with anisotropic thermal parameters. All the hydrogen atoms were geometrically fixed and allowed to refine using a riding model. Absorption correction was employed using psi-scan ($T_{max} = 1.000$, $T_{min} = 0.946$). A perspective view (ORTEP [26]) of **5** is illustrated in Fig. 1 showing the atom numbering scheme. Selected bond lengths and angles are given in Table 2.

3. Results and discussion

The ligand N,N'-dimethyl,N,N'-bis(diphenylphosphino)ethylenediamine reacts with Group 6 tetracarbonyl derivatives of the type $[M(CO)_4L_2]$ (M = Cr, Mo, L_2 = norbornadiene, M = W, L_2 = (piperidine)$_2$) to give *cis*-chelated tetracarbonyl derivatives **2**–**4** in good yield. The seven-membered metallacycles are characterized by elemental analyses, infrared and NMR spectroscopic data. The infrared spectra exhibit strong ν(CO) absorptions in the range of 1980–2071 cm^{-1}, characteristic of the bis(phosphine) bound $[M(CO)_4]$ moiety in a *cis* fashion [27]. The ^{31}P-NMR spectra of complexes **2**–**4** exhibit a single resonance, which is considerably deshielded compared to that of the free ligand. The tungsten complex exhibits a $^1J_{PW}$ value of 284 Hz.



2 M=Cr, **3** M=Mo, **4** M=W



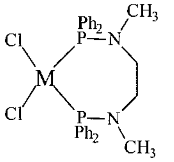
5

The reaction of ligand **1** with an equimolar ratio of Re(I) derivative, $[ReBr(CO)_3(NCMe)_2]$ affords a seven-membered chelate complex, $[ReBr(CO)_3\{Ph_2PN(Me)CH_2CH_2(Me)NPPh_2\}]$ (**5**) with the elimination of two acetonitrile groups. The IR spectrum of **5** shows ν(CO) bands at 1913, 1953 and 2032 cm^{-1} indicating the presence of three carbonyl groups. The ^{31}P-NMR spectrum shows a single resonance at δ 91.6 with a coordinate shift of 29.7 ppm. Further, the structure of this mononuclear complex was confirmed by

Table 2
Selected bond distances (Å) and bond angles (°) for $[Re(CO)_3Br\{PPh_2N(Me(CH_2CH_2(Me)NPPh_2\}]$ (**5**)

Bond distances			
Re(1)–C(1)	1.906(6)	P(2)–C(51)	1.824(6)
Re(1)–C(3)	1.939(7)	P(2)–C(41)	1.841(6)
Re(1)–C(2)	1.949(6)	N(1)–C(13)	1.459(8)
Re(1)–P(1)	2.4884(15)	N(1)–C(11)	1.462(8)
Re(1)–P(2)	2.5263(14)	N(2)–C(14)	1.480(8)
Re(1)–Br(1)	2.6770(7)	N(2)–C(12)	1.483(8)
P(1)–N(1)	1.669(5)	C(1)–O(1)	1.150(8)
P(1)–C(21)	1.827(6)	C(2)–O(2)	1.136(8)
P(1)–C(31)	1.836(6)	C(3)–O(3)	1.155(8)
P(2)–N(2)	1.703(5)	C(11)–C(12)	1.506(9)
Bond angles			
C(1)–Re(1)–C(3)	91.3(2)	N(1)–P(1)–Re(1)	114.39(19)
C(1)–Re(1)–C(2)	88.6(2)	C(21)–P(1)–Re(1)	111.7(2)
C(3)–Re(1)–C(2)	89.7(3)	C(31)–P(1)–Re(1)	118.6(2)
C(1)–Re(1)–P(1)	90.67(17)	N(2)–P(2)–C(51)	102.5(3)
C(3)–Re(1)–P(1)	177.66(19)	N(2)–P(2)–C(41)	103.7(3)
C(2)–Re(1)–P(1)	91.5(2)	C(51)–P(2)–C(41)	103.4(3)
C(1)–Re(1)–P(2)	87.09(17)	N(2)–P(2)–Re(1)	120.13(18)
C(3)–Re(1)–P(2)	86.23(19)	C(51)–P(2)–Re(1)	104.7(2)
C(2)–Re(1)–P(2)	174.03(19)	C(41)–P(2)–Re(1)	119.87(19)
P(1)–Re(1)–P(2)	92.69(5)	C(13)–N(1)–C(11)	114.3(5)
C(1)–Re(1)–Br(1)	171.91(17)	C(13)–N(1)–P(1)	123.3(4)
C(3)–Re(1)–Br(1)	85.52(18)	C(11)–N(1)–P(1)	122.2(4)
C(2)–Re(1)–Br(1)	83.94(18)	C(14)–N(2)–C(12)	107.5(5)
P(1)–Re(1)–Br(1)	92.64(4)	C(14)–N(2)–P(2)	117.8(4)
P(2)–Re(1)–Br(1)	100.11(4)	C(12)–N(2)–P(2)	116.9(4)
N(1)–P(1)–C(21)	105.8(3)	O(1)–C(1)–Re(1)	175.2(5)
N(1)–P(1)–C(31)	104.2(3)	O(2)–C(2)–Re(1)	176.5(6)
C(21)–P(1)–C(31)	100.5(3)	O(3)–C(3)–Re(1)	179.2(6)
		N(1)–C(11)–C(12)	114.3(5)

single crystal X-ray analysis. Treatment of $[MCl_2(COD)]$ (M = Pd or Pt) with 1:1 molar proportions of the ligand **1** in dichloromethane afford the chelate complexes **6** and **7** in good yield. The ^{31}P-NMR spectra of **6** and **7** exhibit single resonance at δ 79.4 and δ 55.7, respectively, with the platinum complex showing a $^1J_{PtP}$ coupling of 4024 Hz which is consistent with the proposed *cis*-geometry [12,28].



6 M=Pd, **7** M=Pt

The structure of the rhenium complex, **5**, has been determined by single crystal X-ray diffraction studies. Perspective view of the molecule and the numbering scheme are shown in Fig. 1 with selected bond lengths and bond angles in Table 1. The rhenium center is in a typical octahedral environment with two phosphorus atoms and two carbonyls in the plane with remaining CO and the bromide being in axial positions. The two Re–P distances are significantly different as are the two equatorial Re–C distances. The shorter Re–P(1) bond has a shorter Re–C(3) bond and a longer C(3)–O(3) bond *trans* to it and the longer Re–P(2) bond has a longer Re–C(2) bond but a shorter C(2)–O(2) bond *trans* to it suggests a difference in the relative π-acceptor capability of two phosphorus centers with respect to CO but there is no obvious explanation. However, in solution the ^{31}P-NMR spectrum of the compound shows a single resonance indicating the equivalence of both the phosphorus centers. This clearly suggests that the anomaly in the bond distances may result from packing and other solid-state effects. The axial Re–C(1) bond distance is shorter than the average bond distance of equatorial Re–C bond distances by 0.038 Å as expected since it is located *trans* to a weak π-acceptor Br group. The seven-membered chelate ring assumes a boat shape with a P(1)–Re–P(2) angle of 92.69(5)°. The bromide ion is leaning away from the chelate ring with Br–Re–C(2) and Br–Re–C(3) angles of 85.52(18) and 83.94(18)°, respectively, whereas the axial CO do not show any significant change in the bond angles. Interestingly N(1) is virtually planar (sum of angles = 359.8(4)°) but N(2) is distinctly pyramidal (sum of angles = 342.2(4)°). This is accompanied by a slight shortening of the P(1)–N(1) (1.669(5) Å) distance as compared to the P(2)–N(2) (1.703(5) Å) distance and the difference is just above the threshold of crystallographic significance.

4. Conclusions

Metal complexes of bis(phosphine) ligands having heteroatoms in the backbone framework show interesting structural features advocated by both the steric and electronic attributes at the donor phosphorus centers as well as the spacer atoms. The two nitrogen atoms in the rhenium(I) complex exhibit different geometries. Some of these complexes can be further used in designing novel homo- or heterobimetallic complexes [29,30] and high nuclearity clusters and also as catalysts for organic transformations.

5. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 156309. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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