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Synthesis of group 6 metal carbonyl complexes containing 2-diphenylphosphinopyridine (Ph_2Ppy) and 3,6-bis(diphenylphosphino)pyridazine (dpppz). The molecular structure of $Cr(CO)_5(dpppzO)$ (dpppzO = 3-diphenylphosphino-6-diphenylphospholylpyridazine)

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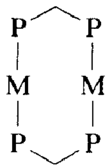
Abstract

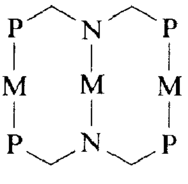
A series of $M(CO)L$, $M(CO)_4L_2$ and $[M(CO)_5]_2L'$ (M = Cr, Mo, W; L = 2-diphenylphosphinopyridine (Ph_2Ppy); L′ = 3,6-bis(diphenylphosphino)pyridazine (dpppz)) complexes were prepared by oxygen atom transfer reaction and their spectra features are discussed. The molecular structure of $Cr(CO)_5$dpppzO (dpppzO = 3-diphenylphosphino-6-diphenylphospholylpyridazine) has been determined by X-ray crystallography. The complex crystallize in the triclinic space group $P\bar{1}$ with two molecules per unit cell of dimensions *a* 10.522(3), *b* 12.487(5), *c* 12.711Å, *α* 109.03(3)°, *β* 100.39(2)° and 94.53(3)°. Full-matrix least-squares refinement yielded *R* 0.060 for 2009 reflections.

Introduction

Bi- and polynuclear complexes in which bi- and multidentate ligands are used to hold more than one metal atom in close proximity have received considerable attention in recent years [1–4]. Such systems generally contain two bridging diphosphines as in **1** and **2**. They have a limited flexibility, however, and this has retricted their chemistry. We have attempted to synthesize novel bi- or polynuclear complexes using singly-bridging 2-diphenylphosphinopyridine (Ph_2Ppy) or 3,6-bis-



(1)



(2)

(3)

(diphenylphosphino)pyridazine (dpppz) ligands. It is anticipated that the phosphorus donor atom will bond to the softer metal and the nitrogen preferentially to the harder metal centre. Recently, some single-bridge systems involving diphosphine such as in **3**, have been described by Shaw [5]. As precursors of these complexes we adopted oxygen atom transfer reaction of $M(CO)_6$ with TMNO(TMNO = Me_3NO) in the presence of the ligand Ph_2Ppy or dpppz in ethyl ether/acetonitrile or acetonitrile to give some new group 6 metal carbonyls having the phosphine ligand. Extensive studies on oxygen atom transfer reaction of metal carbonyls have appeared [6–8].

Results and discussion

Synthesis and spectra

Oxygen atom transfer reaction of $M(CO)_6$ with TMNO in the presence of Ph_2Ppy or dpppz in ether/acetonitrile or acetonitrile proceeds readily at room temperature to give a series of new mono- or disubstituted group 6 mono- or bi-metal carbonyls. The solvent strongly influences the nature of the product. When Ph_2Ppy was the ligand the best solvent was found to be ether/acetonitrile (24 : 1), to give monosubstituted product, but when M = Cr a small quantity of *trans*-disubstituted product was also formed. In acetonitrile the disubstituted product was predominant in spite of the fact that different ratios of $M(CO)_6$, Ph_2Ppy and TMNO were used. With dpppz as ligand ether could not be adopted as solvent because dpppz is insoluble in it. The low yield of the mono-substituted product $[M(CO)_5]_2$dpppz in acetonitrile also shows that the reaction probably favours the formation of multi-substituted product which is difficult to separate.

The elemental analysis and spectroscopic data of these complexes are given in Table 1.

The IR spectra suggest that complexes **5** and **6** possess *cis* structure, but that complex **4** has a *trans* configuration. An absorption at 1200 cm^{-1} indicates that the P=O bond is present in complex **10**.

The ^{31}P NMR spectra show the coordination shifts (δ(complex) – δ(free ligand)) [9] fall in the expected [10] order: for complexes **1**–**3**: Cr(63,40 ppm), Mo(44.81 ppm), W(28.39 ppm); for complexes **7**–**9**: Cr(66.22 ppm); Mo(46.57 ppm), W(29.07 ppm). For tungsten complexes, only the satellites of complex **3** were observed; J(P–W) was 122.07 Hz.

In complexes **1**–**3** and **4**–**6** the differences in the chemical shifts between the mono- and the *cis*-disubstituted carbonyls are very small, whereas a large change is observed between the mono- and *trans*-disubstituted carbonyls in accord with published data [11].

Table 1

Analytical and spectroscopic data for the complexes

Complex	Found(calcd.)(%)			IR	^{31}P	FD-MS
	C	H	N	ν(CO)(cm^{-1})	δ(ppm)	(m/e)
$Cr(CO)_5(Ph_2Ppy)$	58.41	3.16	3.43	2050, 1975, 1930	59.37	
(1)	(58.02)	(3.08)	(3.08)			
$Mo(CO)_5(Ph_2Ppy)$	53.38	2.74	3.20	2050, 1990, 1930	40.78	
(2)	(52.90)	(2.80)	(2.80)			
$W(CO)_5(Ph_2Ppy)$	45.38	2.31	2.56	2050, 1980, 1920	24.36	
(3)	(44.97)	(2.38)	(2.38)		(J(P–W) 122.07 Hz)	
$Cr(CO)_4(Ph_2Ppy)_2$	65.84	4.00	3.59	1940, 1870	75.52	
(4)	(66.08)	(4.06)	(4.06)			
$Mo(CO)_4(Ph_2Ppy)_2$	62.22	3.86	4.27	2010, 1925, 1980	40.52	
(5)	(62.13)	(3.81)	(3.81)	1835		
$W(CO)_4(Ph_2Ppy)_2$	55.48	3.45	3.73	2010, 1910, 1870,	25.03	
(6)	(55.47)	(3.41)	(3.41)	1830		
$[Cr(CO)_5]_2$dpppz	55.60	2.68	3.49	2050, 1980, 1930	59.07	806, 804(100%), 614, 612
(7)	(54.80)	(2.64)	(3.36)			
$[Mo(CO)_5]_2$dpppz	48.91	2.38	3.52	2070, 1990, 1930	39.44	885, 886, 887, 888, 889, 890, 891, 892(100%), 893, 894, 895, 896, 897, 898, 899, 900
(8)	(49.56)	92.39)	(3.04)			
$[W(CO)_5]_2$dpppz	41.94	2.13	2.72	2070, 1980, 1920	21.94	1063, 1064, 1065, 1066, 1067(100%), 1068, 1069, 1070, 1071, 1072, 1073
(9)	(41.60)	(2.00)	(2.55)			
$Cr(CO)_5$dpppzO	60.15	3.32	4.03	2050, 1995, 1920	20.32, 59.90	464, 465, 600, 601, 602, 628(100%), 629, 630, 656, 657, 658
(10)	(60.36)	(3.35)	(4.27)	(1200, ν(P=O))		

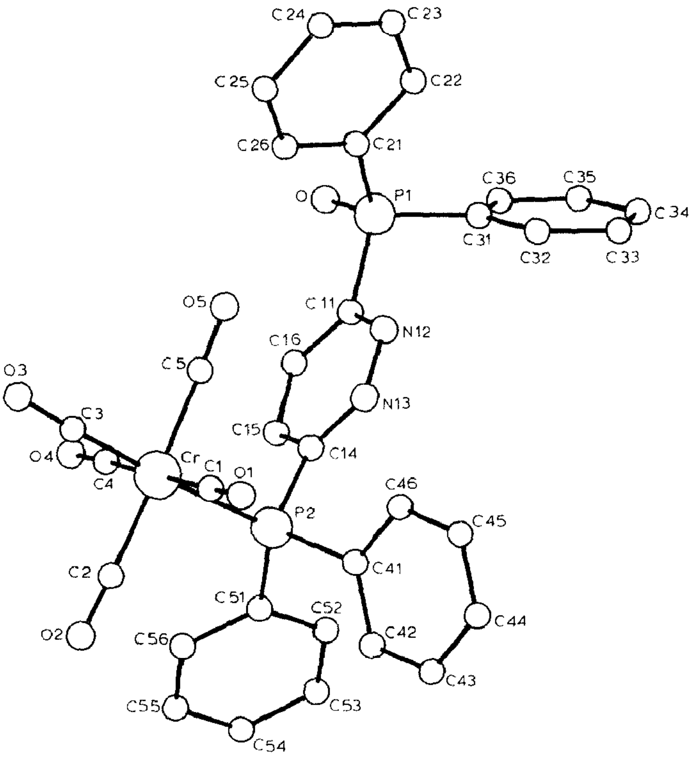


Fig. 1. Structure of $Cr(CO)_5dpppzO$.

Compared with complex 7, the high field shift of the signal from complex **10** may be assigned to the ligated phosphorus, while downfield resonance was due to the oxidized phosphorus.

Field desorption mass spectrometry showed the presence of a group of isotope peaks at $M - 28(CO)$ for complexes 7–9. In addition, a group of peaks at $M - 28(CO) - 192\ [Cr(CO)_5] = 612$ are present in the spectrum of complex 7.

There are four groups of peaks for complex **10** in FD-MS. The process of desorption may be outlined as follows:

$$\underset{(656)}{Cr(CO)_5L} \xrightarrow{-CO} \underset{(628)}{Cr(CO)_4I} \xrightarrow{-CO} \underset{(600)}{Cr(CO)_3L} \xrightarrow{-Cr(CO)_3} \underset{(464)}{L} \quad (L = dpppz\dot{O})$$

Structure of $Cr(CO)_5dpppzO$

The structure of **10** is shown in Fig. 1. Final atomic coordinates and temperature factors are given in Table 2. Selected interatomic distances and angles are listed in Tables 3 and 4, respectively.

The chromium atom exhibits a six-coordinate deformed octahedral configuration. The P–Cr–C(*trans*) angle is 176.7(3)°. According to the π-bonding theory [12] it is expected that the Cr–C(*trans*) distance should be shorter than that of Cr–C(*cis*), whereas the C(*trans*)–O bond is longer than that of C(*cis*)–O one. Our results are as follows: Cr–C(*trans*) = 1.804(9)Å, Cr–C(*cis*, av.) = 1.877(4)Å, C(*trans*)–O =

Table 2
Atomic coordinates and temperatures factors for $Cr(CO)_5$dpppzO.

Atom	x	y	z	B_{eq} (Å^2)
Cr1	0.0419(2)	0.4596(1)	0.7601(1)	3.50(4)
P1	-0.2479(2)	-0.0076(2)	0.8740(2)	3.60(6)
P2	0.0593(2)	0.2704(2)	0.6436(2)	2.75(6)
O	-0.1684(6)	-0.0130(6)	0.9800(5)	5.0(2)
O1	-0.1286(9)	0.5029(7)	0.5620(8)	8.5(3)
O2	0.2733(8)	0.5715(7)	0.7073(8)	8.0(3)
O3	0.0100(8)	0.6874(7)	0.9169(7)	6.3(2)
O4	0.2125(8)	0.4234(7)	0.9609(7)	7.2(3)
O5	-0.2006(7)	0.3735(8)	0.8194(8)	8.4(3)
N12	-0.2111(6)	0.0800(6)	0.7121(6)	3.4(2)
N13	-0.1463(7)	0.1369(7)	0.6593(6)	3.5(2)
C1	-0.063(1)	0.4850(9)	0.636(1)	5.0(3)
C2	0.188(1)	0.5270(9)	0.726(1)	5.7(3)
C3	0.0243(9)	0.5990(8)	0.8534(9)	4.1(3)
C4	0.146(1)	0.4343(9)	0.8830(9)	4.4(3)
C5	-0.108(1)	0.4035(9)	0.797(1)	5.0(3)
C11	-0.1486(8)	0.0583(8)	0.8028(7)	3.1(2)
C14	-0.0170(8)	0.1702(7)	0.6993(7)	2.5(2)
C15	0.0534(8)	0.1448(8)	0.7921(8)	3.3(2)
C16	-0.0121(8)	0.0891(8)	0.8470(8)	3.6(2)
C21	-0.3742(9)	0.0812(8)	0.8970(7)	3.4(2)
C22	-0.5060(9)	0.0260(9)	0.8765(8)	4.4(3)
C23	-0.599(1)	0.0996(9)	0.9065(9)	5.0(3)
C24	-0.566(1)	0.217(1)	0.955(1)	6.0(3)
C25	-0.435(1)	0.269(1)	0.976(1)	6.4(4)
C26	-0.341(1)	0.1969(9)	0.947(1)	5.2(3)
C31	-0.3192(9)	-0.1456(8)	0.7762(8)	3.9(3)
C32	-0.395(1)	-0.163(1)	0.6687(9)	5.2(3)
C33	-0.448(1)	-0.277(1)	0.597(1)	8.6(5)
C34	-0.423(2)	-0.368(1)	0.639(1)	9.7(5)
C35	-0.345(2)	-0.349(1)	0.745(1)	9.0(5)
C36	-0.292(1)	-0.238(1)	0.813(1)	6.1(3)
C41	-0.0184(8)	0.2277(7)	0.4935(7)	2.7(2)
C42	0.057(1)	0.2150(8)	0.4106(8)	4.0(3)
C43	-0.005(1)	0.1924(9)	0.2967(9)	5.1(3)
C44	-0.141(10	0.1778(9)	0.2632(8)	4.7(3)
C45	-0.216(1)	0.1917(9)	0.3452(9)	5.0(3)
C46	-0.1569(9)	0.2157(9)	0.4592(8)	4.2(3)
C51	0.2196(8)	0.2214(8)	0.6408(7)	3.1(2)
C52	0.2243(9)	0.1051(8)	0.5838(8)	3.6(2)
C53	0.346(1)	0.0672(9)	0.5835(8)	4.5(3)
C54	0.4612(9)	0.1460(9)	0.6393(8)	4.5(3)
C55	0.4558(9)	0.261(1)	0.6960(9)	4.9(3)
C56	0.3353(8)	0.3015(9)	0.6994(9)	3.9(3)

Anisotropically refined atoms are given as the isotropic equivalent thermal parameter, defined as: $\frac{4}{3}[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$

1.176(8)Å and C(*cis*, av.)–O = 1.143(6)Å. The Cr–P distance (2.386(2)Å) is shorter than the corresponding distance in $Ph_3PCr(CO)_5$, 2.422(1)Å [13] and longer than that in $(PhO)_3PCr(CO)_5$, 2.309(1)Å [13]. The P–O distance is 1.477(6)Å.

Table 3
Interatomic distances(Å) in Cr(CO)$_5$dpppzO

Cr–P2	2.386(2)	P2–C14	1.827(6)
Cr–C1	1.89(1)	O1–C1	1.152(9)
Cr–C2	1.877(9)	O2–C2	1.122(8)
Cr–C3	1.804(9)	O3–C3	1.176(8)
Cr–C4	1.871(9)	O4–C4	1.158(9)
Cr–C5	1.868(8)	O5–C5	1.139(8)
P1–O	1.477(6)	N12–N13	1.348(7)
P1–C11	1.811(6)	N12–C11	1.339(8)
P1–C21	1.801(7)	N13–C14	1.344(8)
P1–C31	1.772(8)	C11–C16	1.417(9)
P2–C41	1.815(7)	C14–C15	1.417(9)
P2–C51	1.842(6)	C15–C16	1.362(9)

Table 4
Bond angles(Deg) for Cr(CO)$_5$dpppzO

P2–Cr–C1	91.6(3)	O–P1–C31	112.0(4)
P2–Cr–C2	93.9(3)	C11–P1–C21	103.7(3)
P2–Cr–C3	176.7(3)	C11–P1–C31	107.2(3)
P2–Cr–C4	88.3(2)	C21–P1–C31	109.0(4)
P2–Cr–C5	90.3(3)	Cr–P2–C14	107.9(2)
C1–Cr–C2	88.2(4)	Cr–P2–C41	116.2(2)
C1–Cr–C3	90.0(3)	Cr–P2–C51	120.9(3)
C1–Cr–C4	180.1(7)	C14–P2–C41	107.1(4)
C1–Cr–C5	90.0(4)	C14–P2–C51	99.9(3)
C2–Cr–C3	89.2(4)	C41–P2–C51	103.2(4)
C2–Cr–C4	92.8(4)	N13–N12–C11	121.0(5)
C2–Cr–C5	175.6(4)	N12–N13–C14	118.3(5)
C3–Cr–C4	90.0(4)	Cr–C1–O1	178.1(8)
C3–Cr–C5	86.9(4)	Cr–C2–O2	177.2(8)
C4–Cr–C5	90.0(4)	Cr–C3–O3	176.9(7)
O–P1–C11	110.8(3)	Cr–C4–O4	177.2(8)
O–P1–C21	113.8(3)	Cr–C5–O5	177.2(9)

Experimental

General procedure

All reactions were performed under nitrogen by use of Schlenk techniques. The solvents were purified by standard methods. Infrared spectra were recorded on a Shimadzu 435 spectrometer as KBr discs. The ^{31}P NMR spectra were recorded on a JEOL FX-90Q spectrometer at 36.19 MHz using 85% H_3PO_4 as external standard and $CDCl_3$ as solvent. FD-MS were recorded with a Hitachi M-80 spectrometer. Metal hexacarbonyls were purchased from Aldrich Chemical Co. Ph_2Ppy [14], 3,6-dichloropyridazine [15] and TMNO · $2H_2O$ [16] were prepared by published procedures.

Preparation of the ligand 3,6-bis(diphenylphosphino)pyridazine (dpppz)

A solution of 0.1 mol of 3.6-dichloropyridazine in 50 ml of absolute tetrahydrofuran was added dropwise to a solution of 0.2 mol of Ph_2PLi in 200 ml of absolute tetrahydrofuran, then the mixture was heated to 50–60 °C on a water bath for 3 h. After removing the solvent the residue was dissolved in dichloromethane, then water added to remove the lithium salt. The organic phase was separated off and dried over anhydrous $MgSO_4$ overnight. The solvent was removed and the solid extracted with light petroleum (b.p. 30–60 °C) to remove unchanged raw material. The residue was dissolved in acetone and the solution decolourized by active carbon, filtered, and then the volume of the filtrate was reduced to give a pale yellow solid. Purification was accomplished by recrystallization from acetone/methanol. Yield, 27.6 g (61.2%). M.p. 129–130 °C. ^{31}P NMR: δ −7.13 ppm. Anal. Found: C, 74.98; H, 4.80; N, 6.42. $C_{28}H_{22}N_2P_2$ calcd.: C, 75.00; H, 4.91; N, 6.25%.

Preparation of complexes

$Mo(CO)_5(Ph_2Ppy)$. $Mo(CO)_6$ (0.53 g, 2.0 mmol) was added to a solution of Ph_2Ppy (0.53 g, 2.0 mmol) and $TMNO \cdot 2H_2O$ (0.23 g, 2.0 mmol) in ether (24 ml) and acetonitrile (1 ml). After stirring for 15 h at room temperature the solvent was removed and the residue recrystallized from CH_2Cl_2/hexane to give a white solid. Yield, 2.8 g (79.7%), M.p. 106 °C.

$W(CO)_5(Ph_2Ppy)$ was prepared similarly. Yield. 71%, M.p. 116 °C.

$Cr(CO)_5(Ph_2Ppy)$. By the procedure outlined above, a yellow solution with some yellow precipitate was obtained. The filtrate gave the title complex in 47% yield. M.p. 118 °C.

The yellow precipitate was the *trans*-disubstituted product. Yield, 25%. M.p. 170 °C.

$Mo(CO)_4(Ph_2Ppy)_2$. $Mo(CO)_6$ (0.264 g, 1.0 mmol) was added to a solution of Ph_2Ppy (0.53 g, 2.0 mmol) and $TMNO \cdot 2H_2O$ (0.23 g, 2.0 mmol) in 25 ml of acetonitrile. After stirring for 16 h a pale yellow solid separated. The solid was recrystallized from CH_2Cl_2/CH_3OH to give the pure product. Yield, 0.65 g (88.6%). M.p. 166 °C [17].

$Cr(CO)_4(Ph_2Ppy)_2$ and *$W(CO)_4(Ph_2Ppy)_2$* were obtained similarly. Yield, 76.0% (M.p. 170 °C) and 72.5% (M.p. 229 °C).

$[Cr(CO)_5]_2dpppz$. A solution of $Cr(CO)_6$ (0.44 g, 2.0 mmol), dpppz (0.45 g, 1.0 mmol) and $TMNO \cdot 2H_2O$ (0.23 g, 2.0 mmol) in acetonitrile was stirred for 18 h at room temperature. After filtration the solvent was removed, and the residue was recrystallized from ether/methanol to give a yellow product. Yield, 0.31 g (37.3%). M.p. 174 °C.

$[Mo(CO)_5]_2dpppz$ and *$[W(CO)_5]_2dpppz$* were prepared by a similar procedure. Yield, 36.9% (M.p. 118 °C) and 35.0% (M.p. 139 °C).

$Cr(CO)_5dpppzO$. A yellow single crystal was obtained when the solution of $[Cr(CO)_5]_2dpppz$ in ether was slowly evaporated in air. Analysis confirmed that it was $Cr(CO)_5dpppzO$. M.p. 184 °C.

X-ray data collection for $Cr(CO)_5dpppzO$

A crystal of dimensions 0.3 × 0.3 × 0.3 mm was attached to a thin glass fiber and mounted on an Enraf Nonius CAD 4 diffractometer. The crystal was triclinic with space group $P\bar{1}$. The lattice constants are a 10.522(3), b 12.487(5), c 12.711(3)Å, α 109.03(3)°, β 100.39(2)° and γ 94.53(3)°. On the basis of $Z = 2$ and a volume of 1535.8 $Å^3$, the calculated density is 1.420 g cm^{-3}.

Data collection was carried out by using graphite-monochromatized Mo-K_α(0.71073Å) radiation. Of the 3471 independent reflections collected in the range $2 < \theta < 21$ by a ω–2θ scan technique at room temperature, 2009 reflections with $I > 3\sigma(I)$ were considered and used in the refinement. The corrections for *LP* factors and for absorption based on a series of ψ scans were applied to the data.

The structure was solved by direct method (MULTAN 82). The Cr atom was located from an *E*-map. The coordinates of the remaining non-hydrogen atoms were found from subsequent difference Fourier syntheses. The hydrogen atoms were not included in the refinements. The final refinement by full matrix least-squares method with anisotropic thermal parameters for non-hydrogen atoms was converged to unweighted and weighted factors of 0.060 and 0.067.

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