

Rhodium Iminophosphine Complexes as Efficacious Oxygen Carriers. Crystal Structure of a Representative Dioxygen Adduct*

Carlo A. Ghilardi, Stefano Midollini, Simonetta Moneti, Annabella Orlandini and Giancarlo Scapacci

Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione, CNR, Via J. Nardi, 39-50132 Firenze, Italy

The synthesis, characterization and reactivity of some square-planar rhodium(I) complexes with new bidentate ligands o -Ph₂PC₆H₄CH=NR (R = Et, Prⁿ, Prⁱ or Buⁱ) having NP donor atoms have been investigated. Depending on the steric crowding of the ligands the complexes can reversibly form dioxygen adducts, in organic solvent solutions at room temperature. The oxygenation-deoxygenation cycles, which have been monitored by ³¹P NMR spectroscopy, can be repeated several times with minor loss in the starting material. A reversible adduct is similarly obtained by reaction with CO. The reaction of the dioxygen adduct with SO₂ allows the formation of a sulfate derivative. The molecular structure of the dioxygen complex [Rh(o -Ph₂PC₆H₄CH=NPrⁱ)₂(O₂)]BPh₄ has been determined by a single-crystal diffraction study: triclinic, space group $P\bar{1}$, $a = 17.450(7)$, $b = 16.518(7)$, $c = 9.624(5)$ Å, $\alpha = 92.79(6)$, $\beta = 92.52(7)$, $\gamma = 92.69(7)^\circ$, $Z = 2$, $R = 0.057$. The co-ordination of the metal may be alternatively described as distorted trigonal bipyramidal or distorted octahedral, according to whether the dioxygen molecule is treated as occupying one or two equatorial sites respectively. The two oxygen atoms, which are equidistant from the metal, are 1.436(9) Å apart.

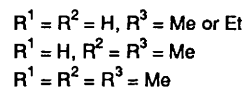
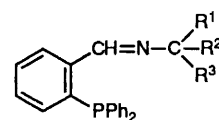
Investigations on transition-metal dioxygen carriers have been stimulated both by their connection with biochemical processes and their great potential for important applications such as oxygen separation and transport.¹ Recently efforts have been devoted to the synthesis of suitably crowded ligands so that the resulting complexes were stable upon dioxygen cycling. In this connection good results were recently achieved with the 'lacunar' Schiff-base complexes where the ligand provides a protected cavity for dioxygen binding.² The numerous families of dioxygen carriers so far proposed principally include cobalt and iron complexes.

We report here the preparation, characterization and study of the reactivity of some rhodium(I) complexes with new bidentate ligands, having NP as donor atoms. This kind of ligand allows modulation of the steric crowding around the metal centre through the simple variation of the alkylimino groups. The compounds have been characterized by standard analytical methods, ¹H and ³¹P NMR spectroscopy. A single-crystal X-ray diffraction analysis was carried out on the dioxygen adduct [Rh(o -Ph₂PC₆H₄CH=NPrⁱ)₂(O₂)]BPh₄, which is, as far as we know, the first rhodium(III) peroxide of a NP ligand system.

The co-ordination of dioxygen to rhodium(I) centres to form both peroxo and superoxo adducts is known and the ability of these complexes to transfer oxygen atoms to both inorganic and organic substrates has been investigated.³

Experimental

All reactions were performed under an atmosphere of dry nitrogen. Solvents were distilled from the usual drying agents prior to use. The starting materials were reagent grade and were used as obtained from their respective suppliers. The ¹H and



³¹P-^{{1}H} NMR spectra were recorded at 200.131 and 81.015 MHz respectively on a Bruker 200-ACP spectrometer. Chemical shifts are relative to internal SiMe₄ (¹H) or external H₃PO₄ (³¹P), with downfield values reported as positive. The ¹H-^{{31}P} NMR spectra were recorded on the same instrument equipped with a 5 mm inverse probe and a BFX-5 amplifier device.

Preparations.—*o*-(Diphenylphosphino)benzaldehyde was prepared according to the reported procedure.⁴ The pure aldehyde was obtained as bright yellow crystals in 80% yield upon recrystallization of the crude product from hot methanol.

The [*o*-(diphenylphosphino)benzylidene]isopropylamine ligand was prepared *via* a Schiff-base reaction carried out under a nitrogen atmosphere. *o*-(Diphenylphosphino)benzaldehyde (1.45 mg, 5 mmol) was added to isopropylamine (25 cm³). The resulting mixture was refluxed for 4 h. The solution was then cooled to room temperature and the crude product was obtained as a powder by distillation of the unreacted isopropylamine. The pure ligand was obtained in 80% yield (1.3 g) upon recrystallization of this powder from degassed hot ethanol (Found: C, 79.15; H, 6.70; N, 4.15. Calc. for C₂₂H₂₂NP: C, 79.75; H, 6.70; N, 4.20%).

The ligands *o*-Ph₂PC₆H₄CH=NEt (Found: C, 79.00; H, 6.30; N, 4.40. Calc. for C₂₁H₂₀NP: C, 79.50; H, 6.35; N, 4.40%), *o*-Ph₂PC₆H₄CH=NPrⁿ (Found: C, 80.00; H, 6.55; N, 4.15. Calc. for C₂₂H₂₂NP: C, 79.75; H, 6.70; N, 4.20%) and *o*-Ph₂PC₆H₄CH=NBuⁱ (Found: C, 79.90; H, 7.00; N, 4.00.

* Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx-xxv.

Table 1 Final positional parameters ($\times 10^4$) for $[\text{Rh}(\text{o-Ph}_2\text{PC}_6\text{H}_4\text{CH}=\text{NPr}^i)_2(\text{O}_2)]\text{BPh}_4$

Atom	x	y	z	Atom	x	y	z
Rh	7202(1)	6983(1)	-438(1)	C(131)	-907(3)	6537(4)	-790(6)
P(1)	6761(1)	8098(1)	797(2)	C(231)	-1044(3)	5697(4)	-888(6)
P(2)	8454(1)	7138(1)	216(2)	C(331)	-526(3)	5204(4)	-1541(6)
O(1)	7615(3)	7199(4)	-2316(5)	C(431)	131(3)	5551(4)	-2095(6)
O(2)	7567(3)	6343(4)	-2111(6)	C(531)	269(3)	6391(4)	-1996(6)
N(1)	6046(4)	6955(4)	-1494(6)	C(631)	-250(3)	6884(4)	-1343(6)
N(2)	6960(4)	6177(4)	1140(7)	C(141)	8807(3)	8191(4)	149(5)
C(1)	5776(5)	7874(5)	1314(8)	C(241)	8991(3)	8678(4)	1353(5)
C(2)	5524(5)	8149(5)	2607(9)	C(341)	9142(3)	9510(4)	1262(5)
C(3)	4770(5)	8004(5)	2966(10)	C(441)	9110(3)	9855(4)	-32(5)
C(4)	4256(5)	7583(5)	2055(10)	C(541)	8926(3)	9368(4)	-1236(5)
C(5)	4473(5)	7332(5)	732(9)	C(641)	8775(3)	8536(4)	-1146(5)
C(6)	5244(5)	7460(5)	364(9)	B	2474(6)	7763(6)	-3561(10)
C(7)	5403(5)	7169(5)	-1043(9)	C(151)	2627(3)	6930(4)	-4538(7)
C(8)	6023(5)	6676(5)	-3017(9)	C(251)	3370(3)	6715(4)	-4820(7)
C(9)	5497(6)	5925(6)	-3272(11)	C(351)	3484(3)	6005(4)	-5614(7)
C(10)	5785(6)	7354(6)	-3941(10)	C(451)	2854(3)	5510(4)	-6125(7)
C(11)	8683(5)	6796(5)	1943(9)	C(551)	2111(3)	5724(4)	-5842(7)
C(12)	9415(6)	7012(6)	2560(11)	C(651)	1997(3)	6434(4)	-5049(7)
C(13)	9625(7)	6757(7)	3906(12)	C(161)	3248(3)	8418(3)	-3528(5)
C(14)	9110(7)	6302(7)	4622(12)	C(261)	3858(3)	8312(3)	-2580(5)
C(15)	8396(7)	6036(7)	3970(12)	C(361)	4507(3)	8840(3)	-2536(5)
C(16)	8170(5)	6290(6)	2623(10)	C(461)	4546(3)	9474(3)	-3440(5)
C(17)	7408(6)	5959(6)	2149(11)	C(561)	3935(3)	9580(3)	-4389(5)
C(18)	6196(6)	5721(6)	1002(10)	C(661)	3286(3)	9051(3)	-4433(5)
C(19)	5785(7)	5756(7)	2381(12)	C(171)	2350(4)	7513(3)	-1893(6)
C(20)	6291(7)	4884(7)	416(13)	C(271)	2277(4)	6708(3)	-1524(6)
C(111)	6626(3)	-1036(3)	-259(5)	C(371)	2154(4)	6531(3)	-147(6)
C(211)	6230(3)	-375(3)	237(5)	C(471)	2102(4)	7159(3)	862(6)
C(311)	6155(3)	298(3)	-570(5)	C(571)	2175(4)	7965(3)	493(6)
C(411)	6475(3)	311(3)	-1872(5)	C(671)	2299(4)	8141(3)	-884(6)
C(511)	6871(3)	-351(3)	-2368(5)	C(181)	1676(3)	8172(3)	-4232(4)
C(611)	6946(3)	-1024(3)	-1561(5)	C(281)	1075(3)	8391(3)	-3404(4)
C(121)	7236(3)	-1519(3)	2431(6)	C(381)	441(3)	8753(3)	-3995(4)
C(221)	7355(3)	-2077(3)	3451(6)	C(481)	407(3)	8895(3)	-5413(4)
C(321)	7776(3)	-1841(3)	4681(6)	C(581)	1008(3)	8675(3)	-6240(4)
C(421)	8080(3)	-1045(3)	4890(6)	C(681)	1642(3)	8314(3)	-5650(4)
C(521)	7962(3)	-487(3)	3870(6)	H(8)	6624(46)	6526(43)	-3227(77)
C(621)	7540(3)	-724(3)	2640(6)	H(18)	5850(38)	6041(40)	228(71)

Calc. for $\text{C}_{23}\text{H}_{24}\text{NP}$: C, 80.00; H, 7.00; N, 4.05%) were prepared analogously using the appropriate amine.

$[\text{Rh}(\text{o-Ph}_2\text{PC}_6\text{H}_4\text{CH}=\text{NPr}^i)_2]\text{BPh}_4$ **1**. To a solution of $[\{\text{Rh}(\text{cod})\text{Cl}\}_2]$ (cod = cycloocta-1,5-diene)⁵ (0.10 g, 0.2 mmol) dissolved in CH_2Cl_2 (5 cm^3) was added the ligand (0.26 g, 0.8 mmol) dissolved in CH_2Cl_2 (15 cm^3). To the resulting red solution was added NaBPh_4 (0.15 g, 0.4 mmol) dissolved in EtOH (15 cm^3). Upon evaporation of CH_2Cl_2 the product was precipitated as a red-brown powder. Red-brown crystals were obtained in 80% yield (0.35 g) by recrystallization from dichloroethane–butanol (Found: C, 75.10; H, 5.90; N, 2.50. Calc. for $\text{C}_{68}\text{H}_{64}\text{BN}_2\text{P}_2\text{Rh}$ **1**: C, 75.30; H, 5.95; N, 2.60%).

Compounds **2–4** were prepared with the same procedure using the ligands $\text{o-Ph}_2\text{PC}_6\text{H}_4\text{CH}=\text{NR}$ (R = Et, Pr^n or Bu^l). Yields: 85, 80 and 80%, respectively (Found: C, 74.95; H, 5.70; N, 2.60. Calc. for $\text{C}_{66}\text{H}_{60}\text{BN}_2\text{P}_2\text{Rh}$ **2**: C, 75.05; H, 5.70; N, 2.65. Found: C, 75.10; H, 5.90; N, 2.50. Calc. for $\text{C}_{68}\text{H}_{64}\text{BN}_2\text{P}_2\text{Rh}$ **3**: C, 75.30; H, 5.95; N, 2.60. Found: C, 75.50; H, 6.10; N, 2.50. Calc. for $\text{C}_{70}\text{H}_{68}\text{BN}_2\text{P}_2\text{Rh}$ **4**: C, 75.55; H, 6.15; N, 2.50%).

$[\text{Rh}(\text{o-Ph}_2\text{PC}_6\text{H}_4\text{CH}=\text{NPr}^i)_2(\text{O}_2)]\text{BPh}_4$ **5**. Dioxygen gas was bubbled through a dichloromethane solution (15 cm^3) of complex **1** (0.4 g, 4 mmol) at room temperature. The solution rapidly changed from red-brown to yellow-orange in a few seconds. Addition of butanol and, under oxygen slow evaporation of the solvent yielded crystals of the adduct **5**. Yield: 0.4 g, 85% (Found: C, 73.00; H, 5.70; N, 2.50. Calc. for $\text{C}_{68}\text{H}_{64}\text{BN}_2\text{O}_2\text{P}_2\text{Rh}$: C, 73.10; H, 5.75; N, 2.50%).

The compounds $[\text{Rh}(\text{o-Ph}_2\text{PC}_6\text{H}_4\text{CH}=\text{NPr}^i)_2(\text{O}_2)]\text{BPh}_4$ **6** and $[\text{Rh}(\text{o-Ph}_2\text{PC}_6\text{H}_4\text{CH}=\text{NPr}^n)_2(\text{O}_2)]\text{BPh}_4$ **7** were prepared

by the same procedure using **2** and **3** as starting material respectively. Yield 80% in each case (Found: C, 72.50; H, 5.50; N, 2.55. Calc. for $\text{C}_{66}\text{H}_{60}\text{BN}_2\text{O}_2\text{P}_2\text{Rh}$ **6**: C, 72.80; H, 5.55; N, 2.55. Found: C, 73.00; H, 5.75; N, 2.50. Calc. for $\text{C}_{68}\text{H}_{64}\text{BN}_2\text{O}_2\text{P}_2\text{Rh}$ **7**: C, 73.10; H, 5.75; N, 2.50%).

$[\text{Rh}(\text{o-Ph}_2\text{PC}_6\text{H}_4\text{CH}=\text{NPr}^i)_2(\text{CO})]\text{BPh}_4$ **8**. Carbon monoxide was bubbled through a solution of complex **1** (0.5 g, 0.46 mmol) in dichloromethane (15 cm^3), at room temperature. The solution changed from red-brown to yellow-orange in minutes. Addition of butanol (20 cm^3) and evaporation of the solvent under carbon monoxide yielded yellow crystals of the CO adduct **8**. Yield: 0.43 g, 85% (Found: C, 74.30; H, 5.80; N, 2.45. Calc. for $\text{C}_{69}\text{H}_{64}\text{BN}_2\text{OP}_2\text{Rh}$: C, 74.45; H, 5.80; N, 2.50%).

$[\text{Rh}(\text{o-Ph}_2\text{PC}_6\text{H}_4\text{CH}=\text{NPr}^i)_2(\text{SO}_4)]\text{BPh}_4$ **9**. The yellow-orange solution of complex **5** (0.4 g, 0.36 mmol) in dichloromethane (15 cm^3) was flushed with sulfur dioxide for a few minutes (ca. 5 min). During this time the solution turned pale yellow. Addition of heptane (15 cm^3) and evaporation of the solvent yielded a yellowish powder of complex **9**. Yield: 0.31 g, 72% (Found: C, 68.95; H, 5.60; N, 2.30. Calc. for $\text{C}_{68}\text{H}_{64}\text{BN}_2\text{O}_4\text{P}_2\text{RhS}$: C, 69.15; H, 5.45; N, 2.35%).

Crystallography for $[\text{Rh}(\text{o-Ph}_2\text{PC}_6\text{H}_4\text{CH}=\text{NPr}^i)_2(\text{O}_2)]\text{BPh}_4$.—*Crystal data*. $\text{C}_{68}\text{H}_{64}\text{BN}_2\text{O}_2\text{P}_2\text{Rh}$, $M = 1116.94$, triclinic, space group $P\bar{1}$, $a = 17.450(7)$, $b = 16.518(7)$, $c = 9.624(5)$ Å, $\alpha = 92.79(6)$, $\beta = 92.52(7)$, $\gamma = 92.69(7)^\circ$, $Z = 2$, $U = 2764.7$ Å³, $D_c = 1.341$ g cm^{-3} , $\lambda = 1.5418$ Å, $\mu(\text{Cu-K}\alpha) = 34.59$ cm^{-1} , $F(000) = 1164$.

Data collection and processing. Yellow-orange prisms, dimen-

Table 2 Hydrogen-1 and phosphorus-31 NMR data^a

Compound	¹ H (δ)	³¹ P- ¹ H (δ)
<i>o</i> -Ph ₂ PC ₆ H ₄ CH=NPr ⁱ ^b	8.88 (d, 1 H, CH=N), 8.00–6.80 (m, 14 H, Ph and C ₆ H ₄), 3.39 [spt, 1 H, CH(CH ₃) ₂ , <i>J</i> (HH) 6], 1.06 [d, 6 H, CH(CH ₃) ₂ , <i>J</i> (HH) 6]	–13.08 (s)
<i>o</i> -Ph ₂ PC ₆ H ₄ CH=NEt ^b	8.90 (d, 1 H, CH=N), 8.20–6.60 (m, 14 H, Ph and C ₆ H ₄), 3.54 (m, 2 H, CH ₂ CH ₃), 1.12 (t, 3 H, CH ₂ CH ₃ , <i>J</i> (HH) 7]	–13.34 (s)
<i>o</i> -Ph ₂ PC ₆ H ₄ CH=NPr ⁿ ^b	8.90 (d, 1 H, CH=N), 8.10–6.80 (m, 14 H, Ph and C ₆ H ₄), 3.46 (m, 2 H, CH ₂ CH ₂ CH ₃), 1.53 (m, 2 H, CH ₂ CH ₂ CH ₃), 0.76 [t, 3 H, CH ₂ CH ₂ CH ₃ , <i>J</i> (HH) 7]	–13.41 (s)
<i>o</i> -Ph ₂ PC ₆ H ₄ CH=NBu ^t ^b	8.82 (d, 1 H, CH=N), 8.10–6.80 (m, 14 H, Ph and C ₆ H ₄), 1.10 [s, 9 H, C(CH ₃) ₃]	–11.66 (s)
[Rh(<i>o</i> -Ph ₂ PC ₆ H ₄ CH=NPr ⁱ) ₂]BPh ₄	8.08 (m, 2 H, CH=N), 7.70–6.80 (m, 48 H, Ph and C ₆ H ₄), 3.87 [spt, 2 H, CH(CH ₃) ₂ , <i>J</i> (HH) 6], 1.48 [d, 6 H, CH(CH ₃)CH ₃ , <i>J</i> (HH) 6], 1.31 [d, 6 H, CH(CH ₃)CH ₃ , <i>J</i> (HH) 6]	52.77 [d, <i>J</i> (RhP) 172]
[Rh(<i>o</i> -Ph ₂ PC ₆ H ₄ CH=NPr ⁱ) ₂ (O ₂)]-BPh ₄ ^c	8.32 [dm, 1 H, CH=N _A , <i>J</i> (PH) 13], 8.27 (m, 1 H, CH=N _B), 7.80–6.20 (m, 48 H, Ph and C ₆ H ₄), 4.74 [spt d, 1 H, C _A H(CH ₃) ₂ , <i>J</i> (HH) 7, <i>J</i> (PH) 2], 4.07 [spt, 1 H, C _B H(CH ₃) ₂ , <i>J</i> (HH) 7], 1.31 [d, 3 H, C _A H(CH ₃)CH ₃ , <i>J</i> (HH) 7], 1.12 [d, 3 H, C _B H(CH ₃)CH ₃ , <i>J</i> (HH) 7], 0.81 [d, 3 H, C _B H(CH ₃)CH ₃ , <i>J</i> (HH) 7], 0.64 [d, 3 H, C _A H(CH ₃)CH ₃ , <i>J</i> (HH) 7]	42.80 [dd, <i>J</i> (RhP) 123, <i>J</i> (PP) 19], 31.60 [dd, <i>J</i> (RhP) 137, <i>J</i> (PP) 19]
[Rh(<i>o</i> -Ph ₂ PC ₆ H ₄ CH=NEt) ₂]BPh ₄	7.97 (m, 2 H, CH=N), 7.60–6.70 (m, 48 H, Ph and C ₆ H ₄), 3.70–3.40 (m, 4 H, CH ₂ CH ₃), 1.43 [t, 6 H, CH ₂ CH ₃ , <i>J</i> (HH) 7]	53.19 [d, <i>J</i> (RhP) 170]
[Rh(<i>o</i> -Ph ₂ PC ₆ H ₄ CH=NEt) ₂ (O ₂)]BPh ₄	8.30–7.85 (m, 2 H, CH=N), 7.70–6.20 (m, 48 H, Ph and C ₆ H ₄), 4.20–3.10 (m, 4 H, CH ₂ CH ₃), 1.20–0.90 (m, 6 H, CH ₂ CH ₃)	41.57 [dd, 1 P, <i>J</i> (RhP) 122, <i>J</i> (PP) 18], 30.16 [dd, 1 P, <i>J</i> (RhP) 138, <i>J</i> (PP) 18]
[Rh(<i>o</i> -Ph ₂ PC ₆ H ₄ CH=NPr ⁿ) ₂]BPh ₄	7.95 (m, 2 H, CH=N), 7.65–6.80 (m, 48 H, Ph and C ₆ H ₄), 3.65–3.25 (m, 4 H, CH ₂ CH ₂ CH ₃), 2.30–1.50 (m, 4 H, CH ₂ CH ₂ CH ₃), 0.70 [t, 6 H, CH ₂ CH ₂ CH ₃ , <i>J</i> (HH) 7]	52.56 [d, <i>J</i> (RhP) 171]
[Rh(<i>o</i> -Ph ₂ PC ₆ H ₄ CH=NPr ⁿ) ₂ (O ₂)]BPh ₄	8.25 (d, 1 H, CH=N), 7.91 (m, 1 H, CH=N), 7.75–6.20 (m, 48 H, Ph and C ₆ H ₄), 4.25–2.90 (m, 4 H, CH ₂ CH ₂ CH ₃), 2.15–1.10 (m, 4 H, CH ₂ CH ₂ CH ₃), 0.72 (m, 6 H, CH ₂ CH ₂ CH ₃)	41.40 [dd, 1 P, <i>J</i> (RhP) 122, <i>J</i> (PP) 18], 29.97 [dd, 1 P, <i>J</i> (RhP) 138, <i>J</i> (PP) 18]
[Rh(<i>o</i> -Ph ₂ PC ₆ H ₄ CH=NBu ^t) ₂]BPh ₄	7.94 (m, 2 H, CH=N), 7.60–6.80 (m, 48 H, Ph and C ₆ H ₄), 1.24 [s, 9 H, C(CH ₃) ₃]	54.14 [d, <i>J</i> (RhP) 177]
[Rh(<i>o</i> -Ph ₂ PC ₆ H ₄ CH=NPr ⁱ) ₂ (CO)]BPh ₄	8.06 (s, 2 H, CH=N), 7.70–6.65 (m, 48 H, Ph and C ₆ H ₄), 3.24 [spt, 2 H, CH(CH ₃) ₂ , <i>J</i> (HH) 7], 0.55 [d, 12 H, CH(CH ₃) ₂ , <i>J</i> (HH) 7]	36 [d, <i>J</i> (RhP) 126]
[Rh(<i>o</i> -Ph ₂ PC ₆ H ₄ CH=NPr ⁱ) ₂ (SO ₄)]-BPh ₄ ^c	8.42 [dm, 1 H, CH=N _A , <i>J</i> (PH) 18], 7.82 (m, 1 H, CH=N), 7.80–6.40 (m, 48 H, Ph and C ₆ H ₄), 5.43 [spt d, 1 H, C _A H(CH ₃) ₂ , <i>J</i> (HH) 6.5, <i>J</i> (PH) 3], 4.12 [spt, 1 H, C _B H(CH ₃) ₂ , <i>J</i> (HH) 6.5], 1.49 [d, 3 H, C _A H(CH ₃)CH ₃ , <i>J</i> (HH) 6.5], 0.96 [d, 3 H, C _B H(CH ₃)CH ₃ , <i>J</i> (HH) 6.5], 0.69 [d, 3 H, C _A H(CH ₃)CH ₃ , <i>J</i> (HH) 6.5], 0.42 [d, 3 H, C _B H(CH ₃)CH ₃ , <i>J</i> (HH) 6.5]	31.40 [dd, 1 P, <i>J</i> (RhP) 114, <i>J</i> (PP) 13], 12.50 [dd, 1 P, <i>J</i> (RhP) 125, <i>J</i> (PP) 13]

^a Chemical shifts δ, coupling constants *J* in Hz, measurements at room temperature in CD₂Cl₂ unless otherwise stated. ^b In CDCl₃. ^c The labels A, B refer to those given in Fig. 2.

sions 0.65 × 0.095 × 0.055 mm; Philips PW 1100 diffractometer, cell constants from 20 randomly selected reflections; ω–2θ scan with scan width = 0.70 + 0.15 tanθ and scan speed 0.05° s⁻¹; graphite-monochromated Cu-Kα radiation, stationary background half the scan time; three standard reflections periodically measured to check the stability of the crystal; standard deviations σ(*I*) calculated according to ref. 6; 4459 reflections measured (5 ≤ 2θ ≤ 90°, ±*h*, ±*k*, +*l*), giving 3773 with *I* ≥ 3σ(*I*); intensities corrected for Lorentz polarization effects and for absorption.⁷

Solution and refinement of the structure. All the calculations were carried out on a SEL 32/77 computer, by using the SHELX 76⁸ and ORTEP⁹ programs. Atomic scattering factors for non-hydrogen atoms were taken from ref. 10 and for hydrogen atoms from ref. 11. Anomalous dispersion terms, both real and imaginary, were included for the non-hydrogen

atoms.¹² The function Σ $w(|F_o| - |F_c|)^2$ was minimized during the least-squares refinements, the weight *w* being defined as 1/σ²(*F*_o). The structure was solved by the heavy-atom method. Full-matrix least-squares refinement was carried out by assigning anisotropic thermal parameters to rhodium, phosphorus, nitrogen and oxygen atoms and by treating the phenyl rings as rigid bodies of *D*_{6h} symmetry. Hydrogen atoms were introduced in their calculated positions, and not refined; H(8) and H(18), which are involved in hydrogen-bonding interactions, were located from a Fourier difference map and successfully refined. The refinement converged into *R* and *R'* of 0.057 and 0.058 respectively. Final positional parameters are reported in Table 1

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

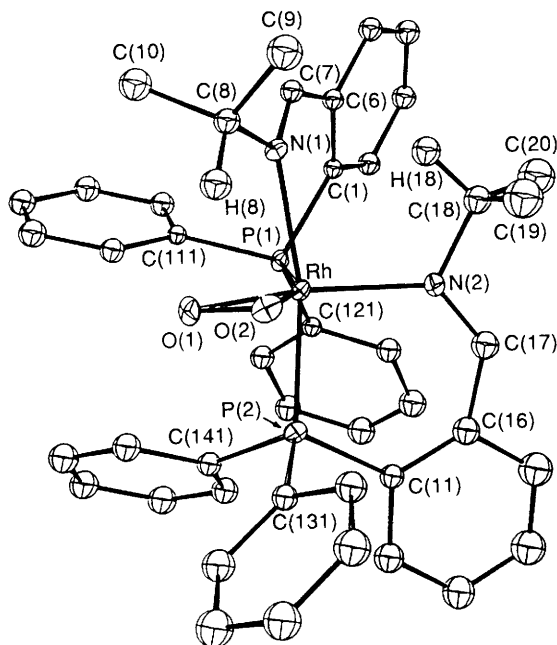


Fig. 1 Perspective view of the complex cation $[\text{Rh}(o\text{-Ph}_2\text{PC}_6\text{H}_4\text{CH}=\text{NPr}^i)_2(\text{O}_2)]^+$: ORTEP drawing with 30% probability ellipsoids

Results and Discussion

The rhodium complexes 1–4 were prepared by reaction of $[\{\text{Rh}(\text{cod})\text{Cl}\}_2]$ with the appropriate NP ligand in the presence of sodium tetraphenylborate in methylene chloride–ethanol solution, using a method analogous to that reported previously.¹³ All the rhodium(I) complexes were isolated as air-stable red-brown crystals. They are moderately soluble in polar organic solvents such as methylene chloride and nitroethane, where they behave as 1:1 electrolytes. The IR spectra show bands in the range 1610–1625 cm^{-1} assigned to the $\nu(\text{C}=\text{N})$ vibrations. The ^1H and ^{31}P NMR spectra (Table 2) suggest a square-planar co-ordination with each phosphorus atom *trans* to a nitrogen atom. Indeed the $^1J(\text{RhP})$ coupling constants (range 170–177 Hz), are similar to those of previously reported square-planar rhodium(I) complexes containing the same donor-atom set.¹³

The complexes 1–3 rapidly react (seconds) at room temperature with dioxygen as evidenced by a change from red-brown to yellow-orange. However, the complex with the more crowded ligand *o*- $\text{Ph}_2\text{PC}_6\text{H}_4\text{CH}=\text{NPr}^i$, 4, is unreactive in oxygenated solutions. The different steric crowding of the NP ligands and therefore the dimensions of the resulting cavity can account for the different reactivity of the complexes towards oxygen.

The reaction of complexes 1–3 with O_2 also occurs, although more slowly, upon exposure of their solutions to air. Crystals of the oxygenated derivatives can easily be obtained by evaporation of the solvent in air. The solids are air stable and soluble in methylene chloride where they behave as 1:1 electrolytes.

A complete X-ray determination of complex 5 established that the molecular structure consists of complex cations $[\text{Rh}(o\text{-Ph}_2\text{PC}_6\text{H}_4\text{CH}=\text{NPr}^i)_2(\text{O}_2)]^+$ and tetraphenylborate anions. A perspective view of the cation is given in Fig. 1. Table 3 reports selected bond distances and angles. The geometry of the cation can be described as distorted trigonal bipyramidal or alternatively distorted octahedral, according to whether the dioxygen molecule is treated as occupying one or two co-ordination sites. In the trigonal-bipyramidal geometry the equatorial positions are occupied by the sideways bonded dioxygen molecule, by the phosphorus [P(1)] and by the nitrogen [N(2)] of two different ligands. The other donor atoms

Table 3 Selected bond distances (Å) and angles ($^\circ$) for $[\text{Rh}(o\text{-Ph}_2\text{PC}_6\text{H}_4\text{CH}=\text{NPr}^i)_2(\text{O}_2)]\text{BPh}_4$

Rh–P(1)	2.322(2)	N(1)–C(7)	1.28(1)
Rh–P(2)	2.245(2)	N(1)–C(8)	1.46(1)
Rh–N(1)	2.216(7)	N(2)–C(17)	1.30(1)
Rh–N(2)	2.111(7)	N(2)–C(18)	1.50(1)
Rh–O(1)	2.016(5)	C(1)–C(6)	1.40(1)
Rh–O(2)	2.026(6)	C(6)–C(7)	1.46(1)
P(1)–C(1)	1.835(8)	C(8)–C(9)	1.51(1)
P(1)–C(111)	1.813(6)	C(8)–C(10)	1.52(1)
P(1)–C(121)	1.817(6)	C(11)–C(16)	1.40(1)
P(2)–C(11)	1.816(9)	C(16)–C(17)	1.46(1)
P(2)–C(131)	1.810(6)	C(18)–C(19)	1.53(1)
P(2)–C(141)	1.823(6)	C(18)–C(20)	1.49(1)
		O(1)–O(2)	1.436(9)
P(1)–Rh–P(2)	98.9(1)	Rh–P(2)–C(131)	115.8(2)
P(1)–Rh–N(1)	83.4(2)	Rh–P(2)–C(141)	111.5(2)
P(1)–Rh–N(2)	93.7(2)	C(11)–P(2)–C(131)	99.8(3)
P(1)–Rh–O(1)	116.0(2)	C(11)–P(2)–C(141)	108.4(3)
P(1)–Rh–O(2)	156.8(2)	C(131)–P(2)–C(141)	106.3(3)
P(2)–Rh–N(1)	167.6(2)	Rh–N(1)–C(7)	130.5(5)
P(2)–Rh–N(2)	93.4(2)	Rh–N(1)–C(8)	114.6(5)
P(2)–Rh–O(1)	81.8(2)	C(7)–N(1)–C(8)	114.8(7)
P(2)–Rh–O(2)	85.0(2)	Rh–N(2)–C(17)	129.0(6)
N(1)–Rh–N(2)	98.7(2)	Rh–N(2)–C(18)	116.3(5)
N(1)–Rh–O(1)	86.3(2)	C(17)–N(2)–C(18)	114.4(7)
N(1)–Rh–O(2)	88.3(2)	P(1)–C(1)–C(6)	119.6(6)
N(2)–Rh–O(1)	150.3(3)	C(1)–C(6)–C(7)	125.5(8)
N(2)–Rh–O(2)	108.9(3)	N(1)–C(7)–C(6)	127.5(8)
O(1)–Rh–O(2)	41.6(3)	N(1)–C(8)–C(9)	110.3(7)
Rh–P(1)–C(1)	109.9(2)	N(1)–C(8)–C(10)	110.0(7)
Rh–P(1)–C(111)	113.3(2)	C(9)–C(8)–C(10)	111.5(8)
Rh–P(1)–C(121)	121.1(2)	P(2)–C(11)–C(16)	121.5(7)
C(1)–P(1)–C(111)	101.1(3)	C(11)–C(16)–C(17)	129.3(9)
C(1)–P(1)–C(121)	102.1(3)	N(2)–C(17)–C(16)	129.3(9)
C(111)–P(1)–C(121)	106.9(2)	N(2)–C(18)–C(19)	111.4(8)
Rh–P(2)–C(11)	114.0(3)	N(2)–C(18)–C(20)	109.8(8)
		C(19)–C(18)–C(20)	114.0(9)

of the ligands [N(1) and P(2)] complete the co-ordination in the axial sites.

While the Rh–O bond distances, which are consistent with the values reported for similar $\text{Rh}(\eta^2\text{-O}_2)$ linkages,¹⁴ appear equivalent [2.016(5) and 2.026(6) Å], the rhodium–phosphorus and –nitrogen bonds show significant variations. In this context it is interesting that the two ligands are not equivalent: one is less tightly bound to the metal displaying M–L distances significantly longer [Rh–P(1) 2.322(2), Rh–N(1) 2.216(7) Å] than the others [Rh–P(2) 2.245(2), Rh–N(2) 2.111(7) Å]; moreover the same ligand is involved in hydrogen bonding with the dioxygen molecule [$\text{H}(8) \cdots \text{O}(1)$ 2.14(7) and $\text{H}(8) \cdots \text{O}(2)$ 1.97(8) Å]. A hydrogen interaction of minor importance [$\text{H}(18) \cdots \text{N}(1)$ 2.32(7) Å] is displayed by the other ligand. Actually one ligand is arranged in such a way that the H(8) atom is almost symmetrical with respect to the dioxygen molecule. This conformation is achieved through a distortion of the six-membered Rh,P(1),N(1) ring, significantly larger than that of the other Rh,P(2),N(2) ring, as evidenced by the displacements [Rh, –1.31; P(1), 0.06; N(1), –0.40; and Rh, 0.52; P(2), 0.02; N(2), 0.21 Å respectively] from the least-squares planes passing through the rings C(1)–C(6) and C(11)–C(16). Further evidence for the different arrangements of the two ligands is provided by the torsion angles C(1)–P(1)–Rh–N(1) (44.1°) and C(11)–P(2)–Rh–N(2) (15.7°). The larger distortions of the Rh,P(1),N(1) ring can account for the longer M–L distances owing to the smaller amount of conjugation.

It is noteworthy that also for the rhodium(I) dioxygen complex $[\text{RhCl}(\text{O}_2)(\text{PPh}_3)_3] \cdot 2\text{CH}_2\text{Cl}_2$ ¹⁵ secondary interactions were taken into account to explain some different values of chemically equivalent bond distances (a contact of 2.0 Å

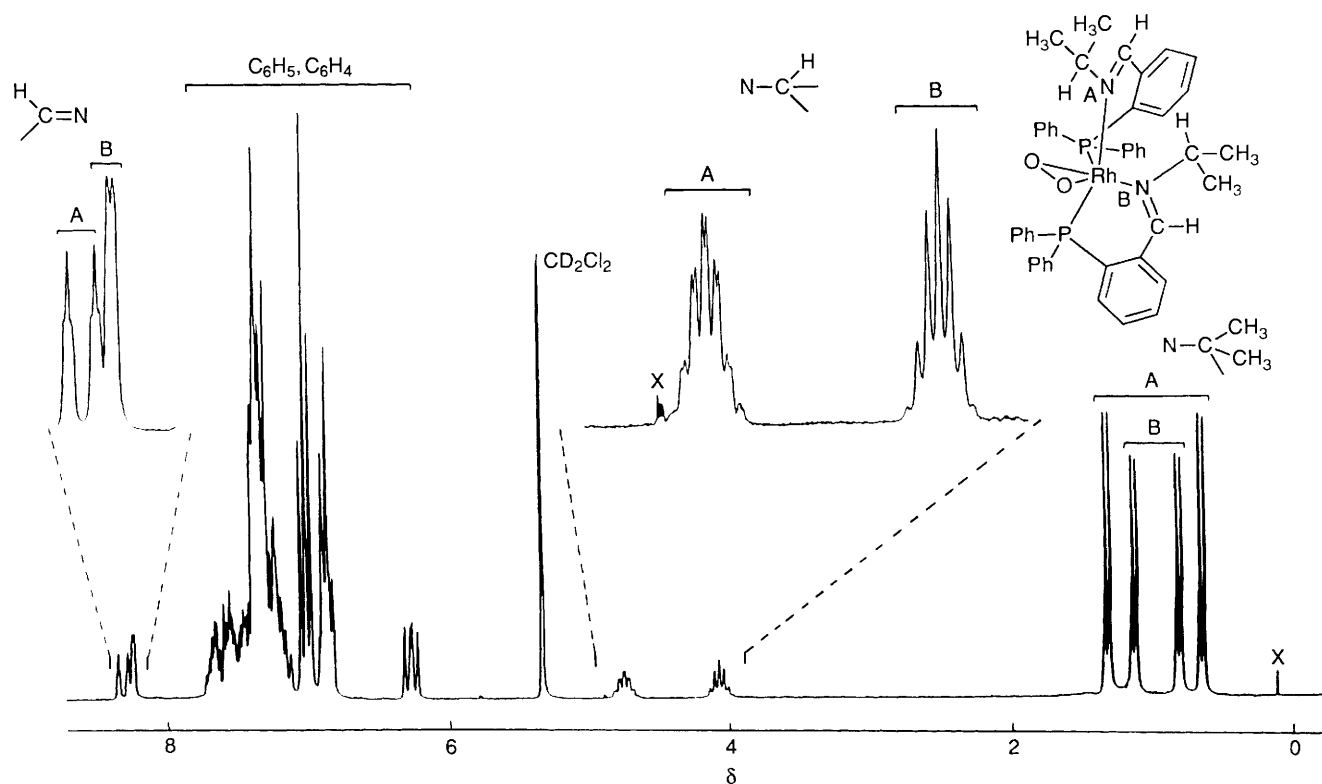


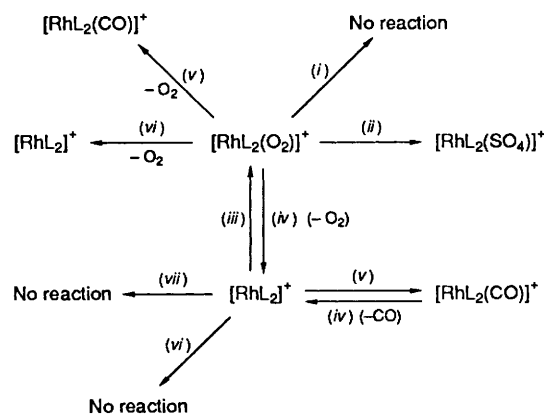
Fig. 2 The ^1H NMR spectrum of $[\text{Rh}(\text{o-Ph}_2\text{PC}_6\text{H}_4\text{CH=NPr}^i)_2(\text{O}_2)]\text{BPh}_4$ (the signals marked X are due to impurities)

between one oxygen and one hydrogen atom of the solvent molecule was found).*

The value of the O(1)–O(2) distance, 1.436(9) Å, falls in the range of values reported for peroxo $\eta^2\text{-O}_2$ transition-metal complexes.¹⁴

The $^{31}\text{P}\{-^1\text{H}\}$ and ^1H NMR spectra of complex **5** (Table 2, Fig. 2) are fully consistent with the pseudo-octahedral geometry found in the solid state. The ^{31}P NMR spectrum is consistent with an AMX spin system. The two signals of the two phosphorus atoms are shifted to high field in comparison with the phosphorus resonance in **1**; the signal at δ 42 may be assigned to the phosphorus in *trans* position to the nitrogen atom. The decrease in magnitude of the $^1J(\text{RhP})$ coupling constant is that expected when passing from a square-planar rhodium(I) to an octahedral rhodium(III) complex.¹⁷ The $^2J(\text{PP})$ coupling constant is consistent with the *cis* relation of the two phosphorus atoms.¹⁷ Concerning the ^1H NMR spectrum (Fig. 2) the signals due to the two isopropyl protons show different features: a septet at δ 4.07 and a septet of doublets at δ 4.74. Analogously the resonances attributable to the two CH=N protons appear respectively as a multiplet (δ 8.27) and a doublet of multiplets (δ 8.32). The $^1\text{H}\{-^{31}\text{P}\}$ NMR spectrum showed that the splitting of the signals at δ 4.74 and 8.32 is due to the coupling to a phosphorus atom. Likely, the split signals can be attributed to the protons belonging to the CH=N–CH group *trans* to the phosphorus atom. Then homonuclear decoupling allowed the assignment of the methyl-proton resonances. The ^{31}P NMR spectra of complexes **6** and **7** are similar (Table 2); the corresponding ^1H NMR spectra (Table 2), although analogous to that of **5**, are more complex and the complete assignment needs further work.

All the oxygenation reactions can be suitably monitored by $^{31}\text{P}\{-^1\text{H}\}$ NMR spectroscopy. The formation of the oxygenated species appears quantitative. Bubbling of nitrogen or argon throughout the oxygenated solutions restores the colour of the



Scheme 1 L = *o*-Ph₂PC₆H₄CH=NR ligand. (i) Excess of PPh₃; (ii) SO₂; (iii) O₂; (iv) Ar; (v) CO; (vi) CO₂; (vii) H₂

starting materials showing the reversibility of the processes. A typical experiment performed at 25 °C on a methylene chloride solution of complex **1**, in the presence of $[\text{N}(\text{PPh}_3)_2]\text{Cl}$ as a standard, has shown that: (i) the quantitative formation of the dioxygen adduct is nearly immediate; (ii) no other measurable species containing phosphorus is formed during the process; (iii) deoxygenation by moderate bubbling of argon throughout the solution is practically complete in *ca.* 20 min; (iv) heating favours the deoxygenation of the complex (at 10 °C after 20 min of argon bubbling only 25% of the complex is deoxygenated) but at >25 °C increasing decomposition occurs; (v) the cycle can be repeated several times with minor loss of the starting complex. After 30 d the overall decomposition of the oxygenated solution at room temperature was *ca.* 25%.

The reactivity of the isolated complexes towards other reagents such as CO, SO₂, CO₂, H₂ and PPh₃ has also been briefly investigated (Scheme 1). When CO is bubbled, at room temperature, though a methylene chloride solution of complex **1** (compounds **2** and **3** show the same reactivity) the colour slowly

* The C–H bond oxidation of an isopropyl group in a metal complex by co-ordinated molecular oxygen has been reported.¹⁶

changes from red-brown to yellow. Crystals of the CO adduct, **8**, can be obtained by evaporation of the solvent under a current of CO. Both the ^1H and $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra of **8** in CH_2Cl_2 solution (Table 2) show the equivalence of the two ligands, whereas the IR spectrum (Nujol mull) with a strong band at 2002 cm^{-1} indicates the presence of a CO group co-ordinated to the metal. These data are consistent with a square-pyramidal geometry. The reaction is easily reversed by bubbling nitrogen or argon through the solution.

The oxygenated complex **5** rapidly reacts with SO_2 , at room temperature, in dichloromethane solution, to form a yellow solution from which **9** can be isolated as a yellowish powder. The compound is air stable. The ^1H and $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra, which are closely related to those of **5**, likely indicate a pseudo-octahedral geometry. On the other hand a set of IR absorptions at 1264 , 1154 , 897 and 655 cm^{-1} are consistent with the presence of a bidentate sulfate ligand.¹⁸ The oxidation of SO_2 is a common reaction for low-valent dioxygen complexes.¹⁹

Complex **1** does not react, at room temperature and atmospheric pressure, with H_2 . Bubbling of CO_2 and CO through solutions of **5** results in recovery of the starting material and formation of the complex $[\text{Rh}(o\text{-Ph}_2\text{PC}_6\text{H}_4\text{CH}=\text{NPr}^i)\text{(CO)}]^+$ respectively.

The reaction of complex **5** with an excess of PPh_3 in methylene chloride solution under oxygen (1 atm, ca. 10^5 Pa) at room temperature yields only a negligible amount of phosphine oxide.

Acknowledgements

We are grateful to Mr. F. Nuzzi for elemental analyses and to Mr. F. Ceconi and P. Innocenti for technical assistance. This work has been partially supported by the Progetto Finalizzato-Chimica Fine, CNR, Rome.

References

- 1 K. A. Lance, K. A. Goldsby and D. H. Busch, *Inorg. Chem.*, 1990, **29**, 4537 and refs. therein; D. Chen and A. E. Martell, *Inorg. Chem.*, 1987, **26**, 1026.
- 2 N. Herron, L. L. Zimmer, J. J. Grzybowski, D. J. Olszowski,

- S. C. Jackels, R. W. Collahan, J. H. Cameron, G. C. Cristoph and D. H. Busch, *J. Am. Chem. Soc.*, 1983, **105**, 6585; R. Delgado, M. W. Glogawski and D. H. Busch, *J. Am. Chem. Soc.*, 1987, **109**, 6855 and refs. therein.
- 3 C. Bianchini, C. Mealli, A. Meli, D. M. Proserpio, M. Peruzzini, F. Vizza and P. Frediani, *J. Organomet. Chem.*, 1989, **369**, C6; C. Bianchini, P. Frediani, F. Laschi, A. Meli, F. Vizza and P. Zanello, *Inorg. Chem.*, 1990, **29**, 3402; H. Mimoun, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, Pergamon, Oxford, 1987, vol. 6, p. 317.
- 4 J. E. Hoots, T. B. Rauchfuss and D. A. Wroblewski, *Inorg. Synth.*, 1982, **21**, 175.
- 5 J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 1957, 4735.
- 6 P. W. R. Corfield, R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, 1967, **6**, 197.
- 7 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
- 8 G. M. Sheldrick, SHELX 76, System of Computing Programs, University of Cambridge, Cambridge, 1976.
- 9 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
- 10 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, p. 99.
- 11 R. F. Stewart, E. R. Davidson and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.
- 12 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, p. 149.
- 13 T. L. Marxen, B. J. Johnson, P. V. Nilsson and L. H. Pignolet, *Inorg. Chem.*, 1984, **23**, 4663.
- 14 M. Laing, M. J. Nolte and E. Singleton, *J. Chem. Soc., Chem. Commun.*, 1975, 660 and refs. therein; M. H. Gubelmann and A. F. Williams, *Struct. Bonding (Berlin)*, 1983, **55**, 1 and refs. therein; H. A. O. Hill and D. G. Tew, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, Pergamon, Oxford, 1987, vol. 2, p. 314 and refs. therein.
- 15 M. J. Bennet and P. B. Donaldson, *Inorg. Chem.*, 1977, **16**, 1581.
- 16 N. Kitajima, M. Osawa, M. Tanaka and Y. Moro-oka, *J. Am. Chem. Soc.*, 1991, **113**, 8952.
- 17 P. S. Pregosin and R. W. Kunz, ^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes, eds. P. Diehl, E. Fluck and R. Kosfold, Springer, Berlin, Heidelberg, 1979.
- 18 W. O. Siegl, S. J. Lapporte and J. P. Collman, *Inorg. Chem.*, 1971, **10**, 2158.
- 19 H. J. Lawson and J. D. Atwood, *J. Am. Chem. Soc.*, 1989, **111**, 6223; J. S. Valentine, *Chem. Rev.*, **73**, 235.

Received 8th April 1992; Paper 2/01867E