Carbonyl Complexes of Niobium and Tantalum and Evidence of a Niobium Dinitrogen Complex: the Structure of Carbonyldichlorocyclopentadienylbis(dimethylphenylphosphine)tantalum

By **Roger J. Burt** and **G. Jeffery Leigh,*** A.R.C. Unit of Nitrogen Fixation, The University of Sussex, Brighton BN1 9RQ
David L. Hughes, Molecular Structures Department, Rothamsted Experimental Station, Harpenden, Herts. AL5 2JQ

The reactions of $[M(\eta\text{-}C_5H_5)Cl_4]$ (M = Nb or Ta) with tertiary phosphines and other ligands and reduction of the products under carbon monoxide give carbonyls such as $[M(\eta\text{-}C_5H_5)(CO)Cl_2(PR_3)_2]$ (PR_3 = tertiary phosphine), but no N_2 analogues. The crystal and molecular structure of $[Ta(\eta\text{-}C_5H_5)(CO)Cl_2(PMe_2Ph)_2]$ has been determined by the heavy-atom method, using Mo-K_α radiation and 1 591 non-zero reflections. The space group is hexagonal $P6_5$, with $a = 13.661(2)$, $c = 26.420(11)$ Å, and $Z = 6$. At convergence, $R = 0.035\,7$ and $R' = 0.037\,0$. Other carbonyls, such as $[Nb(CO)_2Cl(Me_2PCH_2CH_2PMe_2)_2]$ are easily obtainable by reduction under CO, and the preparation of an impure dinitrogen complex which yields some hydrazine with acid is also described.

In our search for new N_2 complexes in which the dinitrogen can be converted to hydrogenated or alkylated derivatives, we have been naturally attracted by the potential of the transition elements of Group 5. Complexes of Group 6, $[M(N_2)_2(PR_3)_4]$ [PR_3 = monotertiary phosphine or $(PR_3)_2$ = ditertiary phosphine] are known and have co-ordinated N_2 which can be alkylated and protonated.[1] Similarly, in Group 4, various dinitrogen complexes containing $M(\eta\text{-}C_5X_5)_2$ groups (M = Ti or Zr, X = H or Me) are known in which dinitrogen can be protonated.[2] It seemed reasonable to suppose that stable and reactive dinitrogen complexes of Group 5 transition metals of the form $[M(\eta\text{-}C_5X_5)(PR_3)_2(N_2)_2]$ should occur. This paper describes our unsuccessful search for such complexes, and the extensive preparative work which this research entailed. Throughout these researches we attempted to prepare analogous CO and N_2 complexes, and used ν(CO) as the criterion for the likely existence[3] of a parallel N_2 complex.

RESULTS AND DISCUSSION

Initially, we had to develop reliable procedures to prepare $[M(\eta\text{-}C_5H_5)X_4]$ (M = Nb and Ta, X = halide). We achieved this by reaction of the metal pentachlorides with non-reducing cyclopentadienyls such as $[Mg(C_5H_5)_2]$ and $[Sn(C_5H_5)R_3]$ (R = Me or Bu^n). These results have already been published by ourselves and others.[4,5] We have subsequently studied the reactions of the tetrahalides with several potential ligands, and the reduction of the resulting complexes by agents such as amalgamated zinc or magnesium under various conditions.

Reactions with Donors.—The complex $[Nb(\eta\text{-}C_5H_5)Cl_4]$ is soluble in toluene and dichloromethane only to a slight extent; however, it is readily soluble in tetrahydrofuran (thf) giving a red solution. The simple adduct $[Nb(\eta\text{-}C_5H_5)Cl_4(thf)]$ has been isolated from this solution and characterised.[6] The addition of tertiary phosphines causes displacement of the thf giving extremely soluble materials but pure adducts could not be isolated. The complex $[Ta(\eta\text{-}C_5H_5)Cl_4]$ is also soluble in thf and reacts with tertiary phosphines to give greenish yellow products. Pale green complexes of general formula $[Ta(\eta\text{-}C_5H_5)Cl_4(PR_3)]$ were isolated using trimethylphosphine and tricyclohexylphosphine; however, for other phosphines the products are too labile to isolate. The addition of a thf solution of 2,2′-bipyridyl (bipy) to a solution of $[Ta(\eta\text{-}C_5H_5)Cl_4]$ in thf gave a precipitate of the adduct $[\{Ta(\eta\text{-}C_5H_5)Cl_4\}_2(bipy)]$ (4). Attempts to prepare adducts using 1,2-dimethoxyethane as solvent gave the stable complex $[Ta(\eta\text{-}C_5H_5)Cl_4(MeOCH_2CH_2OMe)]$ (1) as the only isolable product.

Reductions using Amalgamated Zinc.—The reduction of $[Nb(\eta\text{-}C_5H_5)Cl_4]$ by amalgamated zinc in dichloromethane in the presence of dimethylphenylphosphine yields the paramagnetic niobium(IV) complex $[Nb(\eta\text{-}C_5H_5)Cl_3(PMe_2Ph)]$ (5), isolated as a dichloromethane solvate. The air-sensitive complex is a dark red microcrystalline solid. The e.s.r. spectrum in dichloromethane solution at room temperature is shown in Figure 1. The spectrum consists of ten lines due to coupling of the 4*d* electron with the ^{93}Nb nucleus ($I = \frac{9}{2}$, 100% abundance). Each of the lines is split into a 1 : 1 doublet indicating hyperfine coupling of the 4*d* electron with the phosphorus nucleus of the single phosphine ligand. The 20-line spectrum is centred at $g = 2.04$ ($A_{Nb} = 119$ G and $A_P = 22$ G).† Similar spectra have been reported for the eight-co-ordinate niobium(IV) complex $[NbCl_4(Me_2PCH_2CH_2PMe_2)_2]$[7] and the six-co-ordinate $[NbCl_4(PBu^i{}_3)_2]$ and $[NbCl_4(thf)(PBu^i{}_3)]$.[8] The e.s.r. spectrum of $[Nb(\eta\text{-}C_5H_5)Cl_3(PMePh_2)]$ (6) shows a basic ten-line pattern; however, the spectrum was of poor quality suggesting contamination with a paramagnetic impurity. Daran *et al.*[9] have reported the synthesis

---

† Throughout this paper: 1 G = 10^{-4} T; 1 atm = 101 325 Pa.

of the related complex $[Nb(\eta\text{-}C_5H_5)Cl_3(Ph_2PCH_2CH_2PPh_2)]\cdot C_6H_5CH_3$ by the reaction of $[Nb(\eta\text{-}C_5H_5)Cl_4]$ with $AlEtCl_2$ in toluene in the presence of 1,2-bis(diphenylphosphino)ethane; the crystal structure of this complex shows[9] the niobium atom to be at the centre of a distorted octahedron.

Reductions using Grignard Magnesium.—The tetracarbonyl complexes $[Nb(\eta\text{-}C_5H_5)(CO)_4]$ and $[Ta(\eta\text{-}C_5H_5)(CO)_4]$ are only obtainable using high-pressure reductive carbonylation[10,11] [equations (1) and (2)] which we were unable to reproduce in our laboratory; the reactions are reported[10,11] to proceed in low yield.

In an attempt to synthesise these compounds by a more convenient low-pressure route the reduction of $[M(\eta\text{-}C_5H_5)Cl_4]$ (M = Nb or Ta) under 1 atm of carbon monoxide was carried out using Grignard magnesium. When the metal complex was of niobium an intractible material was obtained which showed no carbonyl bands in the i.r. spectrum. In the case of M = Ta the residue obtained after filtration and evaporation of the reaction mixture had an i.r. spectrum containing bands in the carbonyl region; however, no pure product could be isolated either by sublimation or by crystallisation.

$$M_2Cl_{10} + Na \xrightarrow[\text{diglyme,}\ [Fe(CO)_5]]{CO} Na[M(CO)_5(diglyme)_2] \xrightarrow[HgCl_2]{Na[C_5H_5]} [M(\eta\text{-}C_5H_5)(CO)_4] \qquad (1)$$

$$M_2Cl_{10} \xrightarrow[\text{thf, CO}]{Na/C_5H_6} [M(\eta\text{-}C_5H_5)(CO)_4] \qquad (2)$$

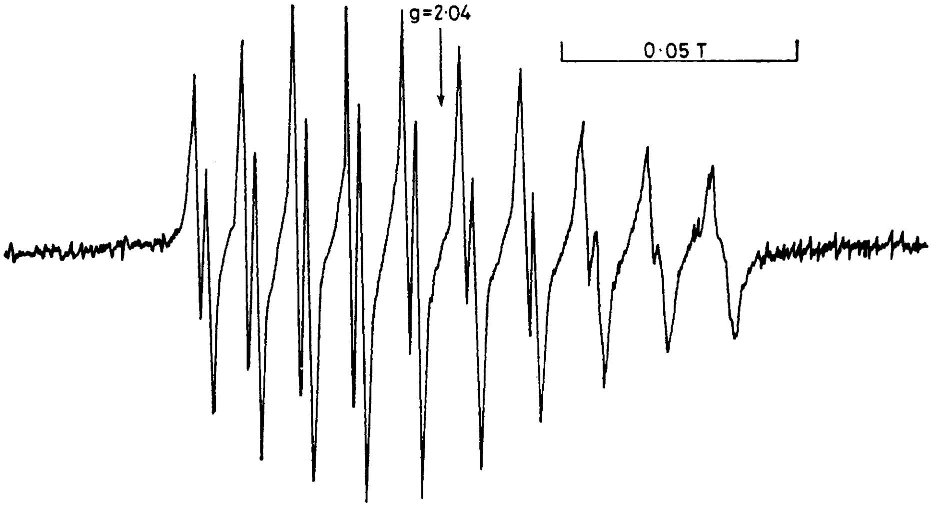

FIGURE 1 E.s.r. spectrum of $[Nb(\eta\text{-}C_5H_5)Cl_3(PMe_2Ph)]\cdot CH_2Cl_2$ in solution in dichloromethane at 20 °C, $g = 2.04$, $(A_{Nb}) = 119$ G, $(A_P) = 22$ G, microwave frequency = 9.126 GHz

The reduction of $[M(\eta\text{-}C_5H_5)Cl_4]$ under CO, using magnesium but in the presence of two equivalents of tertiary phosphine, PR_3, gives complexes of the type $[M(\eta\text{-}C_5H_5)(CO)Cl_2(PR_3)_2]$.[12] The analogous carbonyl complex $[Nb(\eta\text{-}C_5H_5)(CO)Cl_2(Me_2PCH_2CH_2PMe_2)]$ has been reported by Green.[13] The monophosphine complexes are red solids; in the case where M = Ta and PR_3 is dimethylphenylphosphine suitable crystals were obtained for crystallographic examination, the results of which are described below. The complexes were purified by crystallisation from either thf–hexane or dichloromethane–hexane; solutions decompose on standing under dinitrogen to give a white intractible residue which severely hampered purification of these materials by recrystallisation. Yields after purification were therefore very low, in the region of 20%.

The values of ν(CO) (see Experimental section) are such that analogous N_2 complexes are not to be expected. Attempts to reduce these complexes further using sodium amalgam in thf under carbon monoxide or dinitrogen gave only decomposition products. However, Green[13] reported that $[Nb(\eta\text{-}C_5H_5)(CO)Cl_2(Me_2PCH_2CH_2PMe_2)]$ was reduced under carbon monoxide to give $[Nb(\eta\text{-}C_5H_5)(CO)_2(Me_2PCH_2CH_2PMe_2)]$; this class of carbonyl had previously only been obtained[14] by photolysis of $[Nb(\eta\text{-}C_5H_5)(CO)_4]$ in the presence of tertiary phosphines.

We obtained further carbonyl complexes by direct reduction of tertiary phosphine halogeno-derivatives. The complex $[NbCl_4(Me_2PCH_2CH_2PMe_2)_2]$,[15] or a mixture of $[NbCl_4(thf)_2]$ and $Me_2PCH_2CH_2PMe_2$, is reduced by magnesium in thf under CO to give an orange-brown solution from which we isolated $[Nb(CO)_2Cl(Me_2PCH_2CH_2PMe_2)_2]$ in 50% yield. This has ν(CO) (Nujol) at 1 830, 1 820, and 1 760 cm^{-1}. It probably has the same structure as the tantalum analogue of which an *X*-ray study has been made.[7] Reaction with $SiMe_3(NCS)$ leads to decomposition, but it reacts with $SiMe_3(N_3)$ in thf under reflux to give the azido-homologue $[Nb(CO)_2(N_3)(Me_2PCH_2CH_2PMe_2)_2]$ and with LiBr in thf under reflux to yield the bromide $[NbBr(CO)_2(Me_2PCH_2CH_2PMe_2)_2]$. These compounds have ν(CO) at 1 830, 1 820, and 1 765 and at 1 835, 1 825, and 1 765 cm^{-1} respectively although the bromide was characterised by i.r. and mass spectroscopy only. These values of ν(CO) are low enough to suggest that dinitrogen analogues might be stable. The halides could not be replaced by cyclopentadienide or tetraphenylborate. Pure carbonyls with phosphines other than $Me_2PCH_2CH_2PMe_2$ could not be isolated.

Reduction of $[NbCl_4(Me_2PCH_2CH_2PMe_2)_2]$ with magnesium in thf under N_2 yielded a yellow, unstable nitrogen-containing solid. The nitrogen content slowly decreased on standing. The highest nitrogen content approximates to a formulation $[\{NbCl(Me_2PCH_2CH_2PMe_2)_2\}(\mu\text{-}N_2)]$ and there is no band in the i.r. spectrum assignable to ν(NN). Treatment with acid yielded no NH_3, but *ca.* 20% of the nitrogen was converted to hydrazine, the remainder being evolved as N_2. This is consistent with our expectation that dinitrogen complexes of Nb should react with acids to give protonated derivatives, but until better characterised derivatives are available it would be unwise to speculate further. Pure carbonyl or dinitrogen homologues with other tertiary phosphines could not be obtained, although, on the basis of nitrogen analyses, several others exist.

X-*Ray Diffraction Studies of* $[Ta(\eta\text{-}C_5H_5)(CO)Cl_2(PMe_2Ph)_2]\cdot$thf (11).—A view of the tantalum complex molecule, determined by single-crystal analysis of the solvated crystals, is shown in Figure 2. In the crystal form, the molecule shows approximate mirror symmetry, with the P ··· P vector normal to the mirror plane. The cyclopentadienyl ring is aligned accordingly, with C(51) under the Ta–Cl(3) bond, as shown in Figure 2. The Ta co-ordination pattern might be described as a distorted octahedron, but is more easily visualised as derived from the ' four-legged piano stool ' arrangement of the tantalum–benzylidene complex $[Ta(C_5Me_5)(CPh)(PMe_3)_2]$;[16] in our molecule, an extra ligand is bonded in the apical position, *trans* to the cyclopentadienyl ring. Consequently the mean value of the angles cp–Ta–X (where cp is the centroid of the cyclopentadienyl ring, and X is one of the ' legs ') has decreased from 117.1° in the benzylidene complex [16] to 103.8° in our structure.

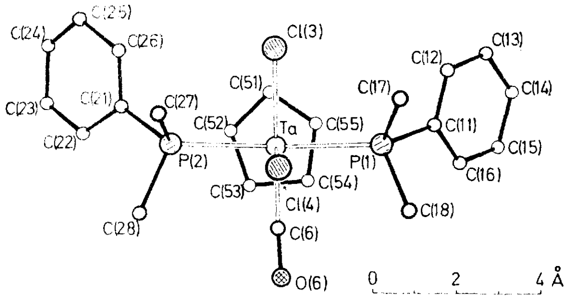

FIGURE 2 Atomic numbering scheme for the complex molecules in $[Ta(\eta\text{-}C_5H_5)(CO)Cl_2(PMe_2Ph)_2]\cdot$thf

Atomic parameters are listed in Table 1 and molecular dimensions are in Tables 2—6.

TABLE 1

Atomic co-ordinates (fractional × 10^4) with estimated standard deviations in parentheses. For solvent atoms, TC, site occupancy factors (s.o.f., × 10^3) are also listed

Atom	*x*	*y*	*z*
Ta	4 590(1)	4 357(1)	1 667.0(0.2)
P(1)	5 718(4)	5 470(4)	2 478(2)
C(11)	4 992(13)	5 189(13)	3 083(5)
C(12)	4 874(13)	4 313(13)	3 389(6)
C(13)	4 283(16)	4 037(18)	3 845(7)
C(14)	3 787(15)	4 653(15)	3 992(6)
C(15)	3 848(15)	5 504(15)	3 687(6)
C(16)	4 439(13)	5 764(13)	3 234(5)
C(17)	6 941(16)	5 308(15)	2 658(6)
C(18)	6 418(15)	7 021(16)	2 421(6)
P(2)	4 655(4)	3 652(4)	740(1)
C(21)	3 560(15)	2 254(15)	546(6)
C(22)	2 677(16)	2 109(18)	216(6)
C(23)	1 827(19)	1 020(19)	92(8)
C(24)	1 935(21)	108(21)	284(8)
C(25)	2 734(19)	190(20)	561(8)
C(26)	3 569(17)	1 300(17)	709(7)
C(27)	5 942(16)	3 586(17)	590(7)
C(28)	4 646(16)	4 603(17)	236(7)
Cl(3)	5 211(4)	2 952(4)	1 911(2)
Cl(4)	6 621(4)	5 550(4)	1 398(2)
C(51)	2 838(20)	2 694(22)	1 977(9)
C(52)	2 674(16)	3 025(17)	1 527(7)
C(53)	2 765(16)	4 101(16)	1 501(6)
C(54)	3 082(17)	4 525(19)	2 000(7)
C(55)	3 119(16)	3 635(17)	2 257(7)
C(6)	4 765(15)	5 809(16)	1 396(6)
O(6)	4 839(13)	6 676(14)	1 254(5)
cp *	2 896	3 596	1 852
H(12)	5 225	3 860	3 277
H(13)	4 222	3 406	4 060
H(14)	3 377	4 484	4 322
H(15)	3 467	5 934	3 793
H(16)	4 467	6 371	3 013
H(22)	2 665	2 782	75
H(23)	1 170	886	−124
H(24)	1 326	−672	192
H(25)	2 771	−491	671
H(26)	4 189	1 392	940
H(51)	2 772	1 960	2 081
H(52)	2 495	2 534	1 221
H(53)	2 637	4 473	1 202
H(54)	3 240	5 273	2 137
H(55)	3 340	3 695	2 621

	x	*y*	*z*	s.o.f.
TC(1)	8 565(47)	1 186(43)	1 600(22)	433(11)
TC(2)	8 022(50)	740(50)	1 863(23)	429(11)
TC(3)	7 764(50)	437(55)	2 160(25)	415(11)
TC(4)	8 792(57)	−124(52)	2 024(25)	418(11)
TC(5)	8 019(55)	−555(55)	1 479(26)	400(11)
TC(6)	9 661(47)	942(51)	2 102(22)	440(11)
TC(7)	9 502(41)	1 346(42)	1 705(21)	438(11)
TC(8)	8 910(58)	282(56)	2 316(24)	413(11)
TC(9)	9 438(56)	886(57)	1 453(27)	338(11)
TC(10)	9 455(53)	565(58)	1 763(30)	336(11)
TC(11)	7 415(57)	234(62)	1 610(30)	329(11)
TC(12)	7 476(45)	−310(46)	1 879(21)	351(11)
TC(13)	8 158(61)	1 108(60)	2 688(29)	260(11)
TC(14)	8 514(62)	640(62)	1 336(28)	271(11)
TC(15)	8 130(69)	−99(64)	2 223(32)	271(11)
TC(16)	9 504(67)	1 566(66)	2 503(35)	254(11)

* cp is the calculated centroid of the cyclopentadienyl ring.

Comparison of co-ordination distances with those of similar molecules is not easy since (*a*) there are few reports of other tantalum(III) structures available, and (*b*) there is considerable crowding of the ligands in our molecule. In $[Ta(\eta\text{-}C_5H_5)_2(Me_2PCH_2CH_2PMe_2)]Cl$[17] the C_5H_5 rings are slightly closer (each 2.035 Å) to the metal atom and the range of Ta–C distances (2.314—2.404 and

2.314—2.395 Å) somewhat smaller than in our complex; in the tetrahedral arrangement here, there seems little steric strain, and the Ta–P distances are *ca.* 2.535 Å.

TABLE 2

Bond lengths (Å), with estimated standard deviations in parentheses

Ta–P(1)	2.633(4)	Ta–C(51)	2.47(2)
Ta–P(2)	2.650(4)	Ta–C(52)	2.24(2)
Ta–Cl(3)	2.539(4)	Ta–C(53)	2.38(2)
Ta–Cl(4)	2.518(4)	Ta–C(54)	2.35(2)
Ta–C(6)	2.01(2)	Ta–C(55)	2.34(2)
		Ta–cp	2.07
P(1)–C(11)	1.82(2)	P(2)–C(21)	1.81(2)
P(1)–C(17)	1.85(2)	P(2)–C(27)	1.85(2)
P(1)–C(18)	1.85(2)	P(2)–C(28)	1.86(2)
C(11)–C(12)	1.38(2)	C(21)–C(22)	1.42(2)
C(11)–C(16)	1.39(2)	C(21)–C(26)	1.38(2)
C(12)–C(13)	1.39(2)	C(22)–C(23)	1.39(3)
C(13)–C(14)	1.38(2)	C(23)–C(24)	1.42(3)
C(14)–C(15)	1.38(2)	C(24)–C(25)	1.27(3)
C(15)–C(16)	1.39(2)	C(25)–C(26)	1.42(3)
C(51)–C(52)	1.33(2)	C(6)–O(6)	1.20(2)
C(51)–C(55)	1.36(3)		
C(52)–C(53)	1.41(3)		
C(53)–C(54)	1.42(2)		
C(54)–C(55)	1.42(3)		

In the Ta^V–benzylidene complex (above),[16] where the cyclopentadienyl ring is slightly further (2.13 Å) from the metal, the additional bulkiness of the pentamethyl substituents of the cyclopentadienyl ligand appears to have a greater effect on the Ta–cp distance than that of the higher oxidation state of the metal; the Ta–P distances here are, as expected, longer than in the case above, at *ca.* 2.567 Å. Our values for the Ta–P distances, 2.633 and 2.650 Å, reflect the crowding of ligands about the metal atom.

Values of Ta^V–Cl in the $[TaCl_6]^-$ ion (in the range 2.241—2.354 Å)[18] and in the $[TaCl_5(OEt)]^-$ ion (for the four mutually *trans* Cl groups, each 2.38 Å)[19] would suggest that our Ta–Cl contacts are quite long. A slight lengthening (to *ca.* 2.40 Å) is expected for the change in oxidation state, and the remainder appears to result from steric effects and the *trans* influences of the π bonding in the Ta–(CO) and Ta–(C_5H_5) interactions. The cyclopentadienyl ring is planar, but is considerably distorted from a regular pentagonal shape. The ring angles at C(52) and C(55) are much larger than the others, resulting, presumably, from the proximity of the phosphine phenyl groups; there are some very short interligand contacts, especially those estimated for C(11) · · · H(55) and C(21) · · · H(52) at 2.48 and 2.45 Å. These and other short intramolecular contacts are in Table 5.

TABLE 4

Planes through various groups of atoms, the equations being $lx' + my' + nz' = p$ where x', y', and z' are co-ordinates in orthogonal axes parallel to a, b, and c^*. The root-mean-square deviation of the atoms included in calculating the plane and deviations of other atoms are given in Å

	Atoms in plane	l	m	n	p	Root-mean-square deviation
(*a*)	Ta, Cl(3), Cl(4), C(6), O(6), cp	−0.0479	0.3962	0.9168	6.2458	0.012
(*b*)	P(1), P(2), Cl(3)	0.8752	0.4213	−0.2374	4.7388	
(*c*)	Phenyl ring C(11)—C(16)	−0.5840	−0.6534	−0.4815	−9.8256	0.013
(*d*)	Phenyl ring C(21)—C(26)	0.5939	0.0415	−0.8034	0.9377	0.015
(*e*)	C(51)—C(55)	0.8889	0.3908	−0.2385	1.8284	0.013

Other atoms

(*a*) P(1) −2.52, P(2) 2.56, C(51) 0.096, C(52) 1.05, C(53) 0.64, C(54) −0.77, C(55) 1.01
(*b*) Ta −0.73, Cl(4) 1.75, C(6) −0.49, O(6) −0.40, cp −2.80
(*c*) Ta 2.41, P(1) 0.065, C(17) −1.08, C(18) −1.00
(*d*) Ta −2.31, P(2) −0.03, C(27) 1.35, C(28) 0.69
(*e*) Ta 2.06, P(1) 2.76, P(2) 2.83, Cl(3) 2.87, Cl(4) 4.53, C(6) 2.24

TABLE 3

Bond angles (°), with estimated standard deviations in parentheses

P(1)–Ta–P(2)	147.8(1)	P(2)–Ta–cp	105.6
P(1)–Ta–Cl(3)	84.8(1)	Cl(3)–Ta–Cl(4)	83.4(1)
P(1)–Ta–Cl(4)	73.6(1)	Cl(3)–Ta–C(6)	156.6(5)
P(1)–Ta–C(6)	88.5(5)	Cl(3)–Ta–cp	105.9
P(1)–Ta–cp	106.4	Cl(4)–Ta–C(6)	73.2(5)
P(2)–Ta–Cl(3)	82.8(1)	Cl(4)–Ta–cp	170.8
P(2)–Ta–Cl(4)	75.4(1)	C(6)–Ta–cp	97.5
P(2)–Ta–C(6)	91.2(5)		
C(11)–P(1)–C(17)	100.3(7)	C(21)–P(2)–C(27)	101.0(9)
C(11)–P(1)–C(18)	103.2(7)	C(21)–P(2)–C(28)	104.1(8)
C(17)–P(1)–C(18)	100.2(8)	C(27)–P(2)–C(28)	102.7(9)
P(1)–C(11)–C(12)	120.7(12)	P(2)–C(21)–C(22)	121.0(14)
P(1)–C(11)–C(16)	121.8(11)	P(2)–C(21)–C(26)	121.0(14)
C(12)–C(11)–C(16)	117.3(14)	C(22)–C(21)–C(26)	117.9(17)
C(11)–C(12)–C(13)	122.7(17)	C(21)–C(22)–C(23)	119.4(20)
C(12)–C(13)–C(14)	118.3(18)	C(22)–C(23)–C(24)	117.1(23)
C(13)–C(14)–C(15)	120.6(17)	C(23)–C(24)–C(25)	126.1(27)
C(14)–C(15)–C(16)	120.0(17)	C(24)–C(25)–C(26)	116.6(24)
C(15)–C(16)–C(11)	120.9(15)	C(25)–C(26)–C(21)	122.7(19)
C(52)–C(51)–C(55)	100.4(22)	Ta–C(6)–O(6)	176.9(16)
C(51)–C(52)–C(53)	117.0(19)		
C(52)–C(53)–C(54)	103.3(17)		
C(53)–C(54)–C(55)	103.3(18)		
C(54)–C(55)–C(51)	115.9(20)		
Ta–P(1)–C(11)	119.6(5)	Ta–P(2)–C(21)	118.9(5)
Ta–P(1)–C(17)	116.2(6)	Ta–P(2)–C(27)	114.9(6)
Ta–P(1)–C(18)	114.5(5)	Ta–P(2)–C(28)	113.2(6)

The dimensions of the phosphine and carbonyl ligands appear normal. The Ta–P–C angles (mean 116.2°) are somewhat larger than the C–P–C angles (mean 101.9°), and the $P–C_{Ph}$ bonds appear a little shorter than the $P–C_{Me}$ bonds. The phenyl rings are planar within experimental error.

Molecules of the tantalum complex spiral round several screw axes (Figure 3 and Table 6), and are separated by van der Waals interactions (Table 6).

In the solvent regions, which lie tight in around the 6_5

screw axes, we have not been able to connect the 16 'atoms' (Table 1) in chemically reasonable arrangements. The atom TC(13) might be an oxygen atom of the thf molecule in one orientation, being 2.74 Å from O(6); the other 'atoms', given methylene group dimensions, are at reasonable van der Waals distances from the tantalum complex molecules.

TABLE 5

Selected short interligand (intramolecular) distances (Å)

P(1) ··· Cl(4)	3.088	C(21) ··· C(52)	3.252
P(1) ··· C(55)	3.214	C(27) ··· Cl(4)	3.183
P(1) ··· C(6)	3.268	Cl(3) ··· Cl(4)	3.363
C(11) ··· C(55)	3.223	Cl(3) ··· C(51)	3.086
C(17) ··· Cl(4)	3.394	Cl(4) ··· C(6)	2.731
P(2) ··· Cl(4)	3.162	C(53) ··· C(6)	2.571
P(2) ··· C(52)	3.174	C(54) ··· C(6)	2.621
C(11) ··· H(55)	2.48	C(22) ··· H(52)	2.75
C(12) ··· H(55)	2.73	C(28) ··· H(22)	2.64
C(17) ··· H(12)	2.73	C(6) ··· H(53)	2.60
C(21) ··· H(52)	2.45	C(6) ··· H(54)	2.68

It had been suggested[4] that the spectral data are consistent with the carbonyl group *trans* to the cyclopentadienyl ring, but this is obviously not the case. Calculations show that, assuming the co-ordination pattern in the Figures but with the carbonyl C atom placed along the present Ta–Cl(4) vector, it would be *ca.* 2.9 Å from each phosphorus atom. This is prohibitively close.

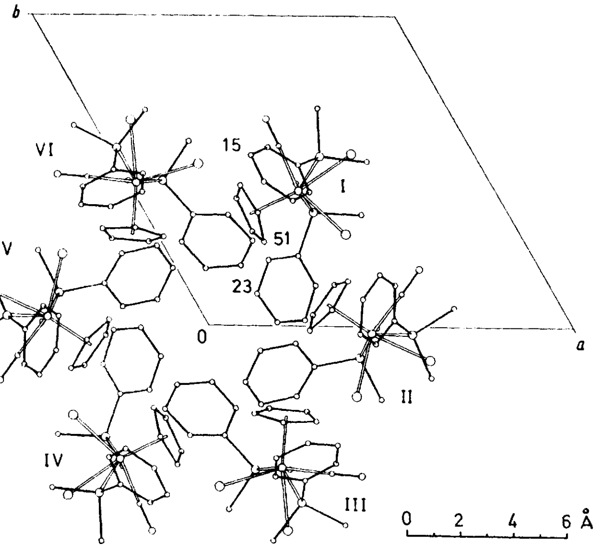

FIGURE 3 Projection of the complex molecules down the hexagonal screw axis (*c* axis); solvent molecules are not shown. The numbers of three carbon atoms are indicated. The symmetry operations denoted by the Roman numerals are listed in Table 6

EXPERIMENTAL

Preparative Studies.—The complexes $[Nb(\eta\text{-}C_5H_5)Cl_4]$ and $[Ta(\eta\text{-}C_5H_5)Cl_4]$ were prepared as described previously.[4] Tertiary phosphines were prepared by standard Grignard methods; trimethylphosphine was prepared by the method of Wolfsberger and Schmidbaur.[20] Grignard magnesium was washed with diethyl ether and dried *in vacuo* before use. Solvents were purified and dried by standard methods and distilled in an atmosphere of dinitrogen before use. All reactions were carried out under an atmosphere of dinitrogen or carbon monoxide using standard Schlenk techniques.

Tetrachloro(η-*cyclopentadienyl*)(1,2-*dimethoxyethane*)-*tantalum* (1).—A pale yellow solution was obtained by dissolving $[Ta(\eta\text{-}C_5H_5)Cl_4]$ (0.65 g, 1.7 mmol) in 1,2-dimethoxyethane (30 cm³). After 2 h a pale yellow precipitate of the *adduct* was filtered off and dried *in vacuo*. Yield 0.2 g (25%) (Found: C, 22.3; H, 2.15. $C_9H_{15}Cl_4O_2Ta$ requires C, 22.6; H, 3.15%).

Tetrachloro(η-*cyclopentadienyl*)(*trimethylphosphine*)-*tantalum* (2).—Trimethylphosphine (0.28 g, 3.6 mmol) was added to $[Ta(\eta\text{-}C_5H_5)Cl_4]$ (0.71 g, 1.8 mmol) suspended in thf (30 cm³). The mixture changed from yellow to green and all solid material dissolved. The solution was concentrated *in vacuo* and filtered to give a pale yellow *solid*. Yield 0.51 g (61%) (Found: C, 21.1; H, 2.90. $C_8H_{14}Cl_4PTa$ requires C, 20.7; H, 3.00%).

Tetrachloro(η-*cyclopentadienyl*)(*tricyclohexylphosphine*)-*tantalum–Tetrahydrofuran* (1/1) (3).—To $[Ta(\eta\text{-}C_5H_5)Cl_4]$ (0.97 g, 2.5 mmol) dissolved in thf (80 cm³) was added tricyclohexylphosphine (1.4 g, 5.0 mmol). The resultant orange solution was concentrated *in vacuo* and hexane added to precipitate a yellow amorphous *solid*. The solid was filtered off and dried *in vacuo*. Yield 0.66 g (40%) (Found: C, 43.2; H, 6.25. $C_{27}H_{46}Cl_4OPTa$ requires C, 43.8; H, 6.25%).

TABLE 6

Short intermolecular contacts (Å) between the tantalum complex molecules

a or a_j	b_i or b	$a \cdots b_i$ or $b \cdots a_j$	*i*	*j*
C(11) ···	C(25)	3.799	IIIa	Va
C(12) ···	C(53)	3.702	II	VIa
C(12) ···	C(54)	3.778	II	VIa
C(13) ···	C(54)	3.749	II	VIa
C(14) ···	C(28)	3.775	IVa	IVb
C(15) ···	C(17)	3.783	IIa	VIb
C(26) ···	H(22)	3.08	II	VIa
C(27) ···	H(54)	3.05	VIb	IIa
Cl(3) ···	H(15)	2.94	VIb	IIa
C(18) ···	C(24)	3.789	IIIa	Va
C(18) ···	Cl(4)	3.766	IIa	VIb
C(22) ···	C(25)	3.621	VIa	II
C(23) ···	C(25)	3.761	VIa	II
C(28) ···	Cl(3)	3.746	VIa	II
C(53) ···	H(12)	3.01	VIa	II
C(54) ···	H(13)	3.09	VIa	II

Atoms a and b are in molecule I; the symmetry codes *i* and *j* indicate the co-ordinates of symmetry related molecules: I x, y, z; II, $y, y - x, z + \frac{1}{6}$; IIa $y, 1 + y - x, z + \frac{1}{6}$; III $y - x, -x, z + \frac{1}{3}$; IIIa $1 + y - x, 1 - x, z + \frac{1}{3}$; IV $-x, -y, z + \frac{1}{2}$; IVa $1 - x, 1 - y, z + \frac{1}{2}$; IVb $1 - x, 1 - y, z - \frac{1}{2}$; V $-y, x - y, z + \frac{2}{3}$; Va $1 - y, x - y, z - \frac{1}{3}$; VI $x - y, x, z + \frac{5}{6}$; VIa $x - y, x, z - \frac{1}{6}$; VIb $1 + x - y, x, z - \frac{1}{6}$.

Molecules with symmetry codes in the first column are those drawn in Figure 4 and, with VIa, are related to I by the 6_5 screw axis through the origin; molecules with other symmetry codes are related to I as follows: IIa and VIb by the 6_5 screw axis at $(1,1,z)$; IIIa and Va by the 3_2 screw axis at $(\frac{2}{3}, \frac{1}{3}, z)$; IVa and IVb by the 2_1 screw axis at $(\frac{1}{2},\frac{1}{2},z)$.

μ-*Bipyridyl-bis*[*tetrachloro*(η-*cyclopentadienyl*)*tantalum*] (4).—2,2′-Bipyridyl (0.5 g, 3.2 mmol) was added to a solution of $[Ta(\eta\text{-}C_5H_5)Cl_4]$ (0.5 g, 1.3 mmol) in thf (50 cm³). The mixture was stirred for 16 h during which time a yellow *precipitate* formed. The solid was filtered off and dried *in* *vacuo*. Yield 0.3 g (42%) (Found: C, 25.6; H, 2.15; N, 2.75. $C_{20}H_{18}Cl_8N_2Ta_2$ requires C, 25.8; H, 1.95; N, 3.00%).

Trichloro(η-*cyclopentadienyl*)(*dimethylphenylphosphine*)-*niobium–Dichloromethane* (1/1) (5).—Dimethylphenylphosphine (1.04 g, 7.6 mmol) was added to a stirred suspension of [Nb(η-C_5H_5)Cl_4] (1.13 g, 3.8 mmol) in dichloromethane (25 cm^3) to give a dark red solution. Amalgamated zinc (10 g) was added and the mixture stirred vigorously for 2 h to give an intense red-orange solution. The mixture was filtered and the solvent removed *in vacuo* to give a dark red microcrystalline *solid*. Yield 1.7 g (92%) (Found: C, 34.5; H, 3.90. $C_{14}H_{18}Cl_5NbP$ requires C, 34.5; H, 3.70%).

Trichloro(η-*cyclopentadienyl*)(*methyldiphenylphosphine*)-*niobium–Dichloromethane* (2/1) (6).—This was prepared analogously to (5) and was isolated as a dark red solid (90%) (Found: C, 43.7; H, 4.2. $C_{18.5}H_{19}Cl_4NbP$ requires C, 43.7; H, 3.7%).

Carbonyldichloro(η-*cyclopentadienyl*)*bis*(*trimethylphosphine*)*niobium–Tetrahydrofuran* (1/1) (7).—Trimethylphosphine (0.39 g, 5.2 mmol) was added to a suspension of [Nb(η-C_5H_5)Cl_4] (0.77 g, 2.6 mmol) in thf (30 cm^3) to give a red solution. The reaction mixture was saturated with carbon monoxide and the reaction flask maintained under a slight positive pressure of carbon monoxide. Magnesium (1.0 g) was added and the reaction mixture stirred vigorously for 16 h to give a dark red-brown reaction mixture which was filtered and the solvent removed *in vacuo*. The crude *product* was recrystallised from thf–hexane as dark red crystals. Yield 0.27 g (22%); $\nu(C\equiv O)$ = 1 940 cm^{-1} (Nujol) (Found: C, 38.6; H, 6.25. $C_{16}H_{31}Cl_2NbO_2P_2$ requires C, 39.9; H, 6.50%). ^1H n.m.r. (CD_2Cl_2); δ = 4.96 (t, 5 H), 1.36 (t, 18 H).

Carbonyldichloro(η-*cyclopentadienyl*)*bis*(*triethylphosphine*)-*niobium–Tetrahydrofuran* (1/2) (8).—This was prepared analogously to complex (7) and was isolated as a dark red *solid* after recrystallisation from thf–hexane. Yield 23%, $\nu(C\equiv O)$ = 1 910 cm^{-1} (Nujol) (Found: C, 50.8; H, 7.65. $C_{26}H_{51}Cl_2NbO_3P_2$ requires C, 49.1; H, 8.05%). ^1H n.m.r. (CD_2Cl_2); δ = 5.00 (t, 5 H), 1.8, 1.1 (complex, 30 H). Samples of both (7) and (8) were always contaminated with an unidentified white product into which they apparently decompose in solution.

Carbonyldichloro(η-*cyclopentadienyl*)*bis*(*trimethylphosphine*)*tantalum–Tetrahydrofuran* (2/1) (9).—This was prepared analogously to complex (7) and was isolated as a red *solid* after recrystallisation from thf–hexane. Yield 15%, $\nu(C\equiv O)$ = 1 890 cm^{-1} (Nujol) (Found: C, 31.5; H, 5.15. $C_{14}H_{27}Cl_2O_{1.5}P_2Ta$ requires C, 31.5; H, 5.10%). ^1H n.m.r. ($CDCl_3$); δ = 4.92 (t, 5 H), 1.56 (t, 18 H).

Carbonyldichloro(η-*cyclopentadienyl*)*bis*(*triethylphosphine*)-*tantalum* (10).—This was prepared analogously to (7) and was isolated as a maroon *solid* after recrystallisation from dichloromethane–hexane. Yield 18%; $\nu(C\equiv O)$ = 1 890 cm^{-1} (Nujol) (Found: C, 37.2; H, 5.75. $C_{18}H_{35}Cl_2OP_2Ta$ requires C, 37.2; H, 6.05%). A sample in CD_2Cl_2 decomposed too rapidly for a ^1H n.m.r. spectrum to be obtained.

Carbonyldichloro(η-*cyclopentadienyl*)*bis*(*dimethylphenylphosphine*)*tantalum–Tetrahydrofuran* (1/1) (11).—This was prepared analogously to (7) and was isolated as red *needles* after recrystallisation from thf–hexane. Yield 20%, $\nu(C\equiv O)$ = 1 915 cm^{-1} (Nujol) (Found: C, 44.9; H, 5.50. $C_{26}H_{35}Cl_2O_2P_2Ta$ requires C, 45.0; H, 5.05%). Recrystallisation from dichloromethane–hexane gave a product with one CH_2Cl_2 (Found: C, 40.0; H, 4.35. $C_{23}H_{29}Cl_4O_8P_2Ta$ requires C, 39.1; H, 4.10%). ^1H n.m.r. (CD_2Cl_2); δ = 4.40 (t, 5 H), *ca*. 7.5 (complex, 10 H), 1.84 (t, 6 H), 1.96 (t, 6 H).

Carbonyldichloro(η-*cyclopentadienyl*)*bis*(*triphenylphosphine*)*tantalum* (12).—This was prepared analogously to (7) and isolated as an amorphous labile brown *solid* which could not be obtained in a pure state, $\nu(C\equiv O)$ = 1 895 cm^{-1} (Nujol).

Bis[1,2-*bis*(*dimethylphosphino*)*ethane*]*bis*(*carbonyl*)*chloroniobium* (13).—The complex [$NbCl_4(thf)_2$] (1.18 g, 3.13 mmol) was suspended in thf (40 cm^3) and $Me_2PCH_2CH_2PMe_2$ (0.94 g, 6.26 mmol) added. The blue solution was stirred for 15 min, and then Mg (1.0 g) added under a strong current of CO at atmospheric pressure. After 1 h, the solution was brown-yellow. After a further 2 d stirring, the solution was filtered, and the *residue* evaporated to dryness *in vacuo*. It was recrystallised from thf–hexane. Yield 1.2 g, 80%. The pure product was obtained as bright yellow crystals after chromatography on silica gel using thf as eluant. The mass spectrum has peaks at m/e = 484 (P^+), 456 ($P - CO^+$), and 428 ($P - 2CO^+$). The ^1H n.m.r. spectrum in [$^2H_6$]-dimethyl sulphoxide showed the expected phosphine proton signals. It is a non-conductor in 1,2-dichloroethane solution (Found: C, 34.4; H, 6.10. $C_{14}H_{32}ClNbO_2P_4$ requires C, 34.7; H, 6.65%).

μ-*Dinitrogen-bis*{*bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]-*chloroniobium*} (14).—The complex [$NbCl_4(thf)_2$] (1.26 g, 3.33 mmol) was allowed to react with $Me_2PCH_2CH_2PMe_2$ (1.00 g, 6.66 mmol) in thf (40 cm^3) as above, and reduced with Mg (1.0 g) under a vigorous stream of N_2. After 3 h, the excess of Mg was filtered off the red-brown solution which was evaporated to dryness. This *residue* had the highest nitrogen content of all the materials examined. Attempts to purify the solid by recrystallisation always led to a loss of nitrogen. The impure solid analysed as follows: C, 35.6; H, 8.60; Cl, 6.4; N, 2.45. $C_{24}H_{64}Cl_2N_2Nb_2P_8$ requires C, 32.7; H, 7.25; Cl, 8.0; N, 3.10%. There was no band in the i.r. spectrum assignable to $\nu(N_2)$.

Azidobis[1,2-*bis*(*dimethylphosphino*)*ethane*]*bis*(*carbonyl*)-*niobium* (15).—Compound (13) (0.32 g, 0.66 mmol) was dissolved in thf (20 cm^3) and $SiMe_3(N_3)$ (0.23 cm^3, 1.98 mmol) added. After heating at reflux for 12 h, solvent was removed *in vacuo* yielding a yellow *solid* which was washed with hexane and dried *in vacuo*. Yield 0.22 g, 68% (Found: C, 32.3; H, 6.30; N, 9.10. $C_{14}H_{32}N_3NbO_2P_4$ requires C, 34.2; H, 6.55; N, 8.55%). The compound had a band at 2 120 cm^{-1} in its i.r. spectrum assignable to $\nu(N_3)$.

Crystallographic Studies of [Ta(η-C_5H_5)(CO)Cl_2(PMe_2Ph)$_2$]·C_4H_8O.—*Crystal data*. $C_{22}H_{27}Cl_2OP_2Ta\cdot C_4H_8O$, M = 693.4, Hexagonal, space group $P6_5$, a = 13.661(2), c = 26.420(11) Å, U = 4 270.2 Å^3, Z = 6, D_c = 1.62 g cm^{-3}, $F(000)$ = 2 064, μ(Mo-K_α) = 41.4 cm^{-1}, λ(Mo-K_α) = 0.710 69 Å.

The crystals used for the X-ray diffraction study were obtained by repeated recrystallisation from thf–hexane. The crystals were separated manually from the white amorphous decomposition product which is a by-product of the recrystallisation process. The slightly air-sensitive crystals were deep carmine coloured and were elongated prisms with rhomboid section. A single crystal, length 0.31 mm, cross-section diagonals 0.17 × 0.10 mm, was mounted in a dry dinitrogen atmosphere on a fibre and then coated in epoxy resin. Photographic data indicated hexagonal symmetry, Laue group $6/m$, with the crystal mounted with its c axis coincident with the rotation axis. Precise cell dimensions and the space group ($P6_1$ or $P6_5$) were determined from measurements on an Enraf–Nonius CAD4 diffractometer with monochromated Mo-K_α radiation. Intensity data were measured also on this instrument, with a variable scan speed, moving crystal–moving counter technique in which the scan speed ratio was fixed at the optimal value of 3 : 2; background counts were calculated from the measurements over the first and last sixths of the scan From a θ range of 1—22.5°, intensities of 1 899 unique reflections were recorded; of these, 1 591 had intensity $I > 2\sigma(I)$, and were used in the structure analysis. From series of ψ scans of seven reflections and their symmetry equivalents (total 500 measurements), empirical absorption parameters were determined by the method of Sheldrick *et al.*[21] and the intensity data were scaled accordingly. Lorentz and polarisation corrections were also applied. From frequent measurements of two intensity control reflections, the crystal showed no indication of deterioration.

The determination of the crystal structure was by the heavy-atom method. The Ta atom was located from a Patterson map and structure factors on that atom alone gave $R = 0.21$; the remaining atoms of the tantalum complex were found in electron-density maps. However, a molecule of solvent, thf, appears to be disordered over several orientations and has not been satisfactorily resolved; in the solvent region, the co-ordinates and alternately $U_{\text{iso.}}$ (see SUP 22942) of 16 'atoms' were refined in the least-squares refinement procedure.

In the tantalum complex, the parameters of the hydrogen atoms of the aromatic rings were calculated and allowed to ride on those of the bonded C atoms. The hydrogen atoms of the methyl groups were not located, calculated, or included in the structure-factor calculations. The Ta, P, and Cl atoms were refined with anisotropic thermal parameters, the remainder isotropically.

At convergence, R was 0.0357 and R' 0.0370 for the 1 591 reflections, after refinement in space group $P6_5$, with a weighting scheme $w = 1/\sigma^2(F)$, *i.e.* derived directly from counting measurements. Scattering curves, and factors for anomalous scattering, were taken from ref. 22; for tantalum, the curve for Ta^{5+} was used.

Corresponding refinement in the space group $P6_1$, *i.e.* the enantiomeric system, led to R and R' values of 0.0404 and 0.0435, and the estimated errors in refined parameters were *ca.* 20% higher than those in the $P6_5$ results. We conclude that, for the particular crystal examined, the $P6_5$ results are correct; the atomic parameters in Table 1 and all dimensions quoted are of the molecule of that system.

Measured and calculated structure amplitudes and thermal parameters are in Supplementary Publication No. SUP 22942 (12 pp.).*

Computing.—The principal programs used in this structure analysis were (*i*) the CAD4 processing program,[23] (*ii*) SHELX,[24] and (*iii*) ORTEP,[25] for the diagrams; these programs have been adapted for use on the ICL 4/70 computer at Rothamsted. Smaller, geometrical calculations were computed on an IBM 1130 system, using the XRAY ARC library of programs.[26]

We acknowledge the help and advice of Professor M. R. Truter.

[0/808 *Received*, 28*th May*, 1980]

---

* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1979, Index issue.

REFERENCES

[1] J. Chatt, J. R. Dilworth, and R. L. Richards, *Chem. Rev.*, 1978, 75.

[2] J. M. Manriquez, D. R. McAlister, E. Rosenberg, A. M. Shiller, K. L. Williamson, S. I. Chan, and J. E. Bercaw, *J. Am. Chem. Soc.*, 1978, **100**, 3078.

[3] J. Chatt and G. J. Leigh, *Chem. Soc. Rev.*, 1972, **1**, 121.

[4] R. J. Burt, J. Chatt, G. J. Leigh, J. H. Teuben, and A. Westerhof, *J. Organomet. Chem.*, 1977, **129**, C33.

[5] M. J. Bunker, A. DeCian, and M. L. H. Green, *J. Chem. Soc., Chem. Commun.*, 1977, 59.

[6] J. H. Teuben, personal communication.

[7] S. Datta and S. S. Wreford, *Inorg. Chem.*, 1977, **16**, 1134.

[8] E. Samuel, G. Labauze, and J. Livage, *Nouv. J. Chim.*, 1977, **1**, 93.

[9] J.-D. Daran, K. Prout, A. DeCian, M. L. H. Green, and N. Signaporia, *J. Organomet. Chem.*, 1977, **136**, C4.

[10] R. B. King, *Z. Naturforsch., Teil B*, 1963, **18**, 157.

[11] K. N. Anisimov, N. E. Kolobova, and A. A. Pasynskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1969, 2238.

[12] R. J. Burt and G. J. Leigh, *J. Organomet. Chem.*, 1978, **148**, C19.

[13] M. L. H. Green, personal communication.

[14] N. E. Kolobova and A. A. Pasynskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1966, 2231.

[15] L. E. Manzer, *Inorg. Chem.*, 1977, **16**, 525.

[16] M. R. Churchill and W. J. Youngs, *Inorg. Chem.*, 1979, **18**, 171.

[17] B. M. Foxman, T. J. McNeese, and S. S. Wreford, *Inorg. Chem.*, 1978, **17**, 2311.

[18] D. F. Lewis and R. C. Fay, *Inorg. Chem.*, 1976, **15**, 2219.

[19] J. C. Dewan, D. L. Kepert, C. L. Rawlston, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1975, 2031.

[20] W. Wolfsberger and H. Schmidbaur, *Synth. React. Inorg. Metal-Org. Chem.*, 1974, **4**, 149.

[21] G. M. Sheldrick, G. Orpen, B. E. Reichert, and P. R. Raithby, Abstracts, 4th European Crystallographic Meeting, Oxford, 1977, 147.

[22] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, pp. 99 and 149.

[23] M. B. Hursthouse, Queen Mary College, London, England.

[24] G. M. Sheldrick, SHELX-76, Program for Crystal Structure Determination, University of Cambridge, England.

[25] C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Tennessee, U.S.A.

[26] *J. Appl. Crystallogr.*, 1973, **6**, 309.