Synthesis and Structural Characterization of the Complexes $[Os_3(CO)_{10}(CON_3Ph)(NCMe)]$ and $[Os_3(CO)_{10}(CON_3Ph)(NC_5H_5)]$ †

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The clusters $[Os_3(CO)_{11}(NCMe)]$ and $[Os_3(CO)_{11}(NC_5H_5)]$ have been treated with phenyl azide to give $[Os_3(CO)_{10}(CON_3Ph)(L)]$ [L = NCMe (1) or NC_5H_5 (2)], the structures of which in the solid state were established by *X*-ray crystallography. Complex (1) crystallises in space group $P\bar{1}$ with a = 9.029(3), b = 12.720(5), c = 13.433(5) Å, α = 102.69(2), β = 102.52(2), γ = 104.75(2)°, and Z = 2. The structure was solved by a combination of direct methods and Fourier-difference techniques, and refined by blocked-cascade least squares to R = 0.057 for 3 739 unique diffractometer data. Complex (2) crystallises in the monoclinic space group $P2_1/n$ with a = 9.311(4), b = 16.707(11), c = 20.241(15) Å, β = 101.88(5)°, and Z = 4. The structure was solved using the same techniques as for (1), and refined by blocked-cascade least squares to R = 0.080 for 2 566 diffractometer data. In both complexes the Os atoms define a triangle with one edge extended to be non-bonding [3.612(2) Å in (1) and 3.615(2) Å in (2)]. This long edge is bridged by one of the terminal N atoms of the azide. The N atom at the other end of the azide, bound to the phenyl ring, is co-ordinated to the carbon atom of the adjacent equatorial carbonyl group. The other bridged Os atom has an NCMe group [in (1)] or a NC_5H_5 ligand [in (2)] co-ordinated in an axial site.

Organic azides have been shown [1,2] to react with the unsaturated cluster $[Os_3(\mu\text{-}H)_2(CO)_{10}]$. Proton n.m.r. experiments demonstrate that the nitrogenous ligands of $[Os_3(CO)_{11}(NCMe)]$ and $[Os_3(CO)_{11}(NC_5H_5)]$ are labile in solution suggesting the presence of a reactive intermediate '$[Os_3(CO)_{11}]$' which is also unsaturated; this prompted us to investigate the reactions of these clusters with phenyl azide.

$$[Os_3(CO)_{11}(NCCH_3)] \underset{(ii)}{\overset{(i)}{\rightleftharpoons}} [Os_3(CO)_{11}] \underset{(iv)}{\overset{(iii)}{\rightleftharpoons}} [Os_3(CO)_{11}(NCCD_3)]$$

Scheme. A dissociative mechanism for exchange of co-ordinated acetonitrile: (*i*) $-NCCH_3$; (*ii*) $+NCCH_3$; (*iii*) $+NCCD_3$; (*iv*) $-NCCD_3$

Results and Discussion

The proton n.m.r. spectrum of $[Os_3(CO)_{11}(NCMe)]$ ($CDCl_3$, ambient) contains a resonance at 2.71 p.p.m. (δ values throughout) due to *co-ordinated* $NCCH_3$. Addition of CD_3CN (two drops) causes complete exchange of the co-ordinated acetonitrile in less than 1 h as evidenced by the disappearance of the signal at 2.71 p.p.m. and appearance of a peak at 1.95 p.p.m. due to *free* acetonitrile. Analogous experiments with $[Os_3(CO)_{11}(NC_5H_5)]$ and NC_5D_5 show that the co-ordinated pyridine is displaced in less than 1 h; the 2,6-hydrogen signal for the pyridine is shifted from *ca.* 9.1 p.p.m. to *ca.* 8.6 p.p.m. [$(CD_3)_2CO$, ambient]. One possible explanation for this exchange is an equilibrium of the type shown (Scheme).

A species of formula '$[Os_3(CO)_{11}]$' is a 46-electron, co-ordinatively unsaturated moiety which might be expected to react with azides on the basis of analogy with $[Os_3(\mu\text{-}H)_2(CO)_{10}]$.[1,2] Furthermore, $[Os_3(CO)_{11}(NCMe)]$,[3] $[Os_3H_2(CO)_{10}]$,[4] and $[Os_3(CO)_9(C_2Ph_2)]$ [5] have all been shown to react with another 1,3-dipolar compound, diazomethane.

Reactions of $[Os_3(CO)_{11}(NCMe)]$ and $[Os_3(CO)_{11}(NC_5H_5)]$ in dichloromethane at 20 °C led to the formation of $[Os_3(CO)_{10}(CON_3Ph)(L)]$ [L = NCMe (1) or NC_5H_5 (2)] respectively in *ca.* 5 min [spectral data for complexes (1) and (2) are given in Table 1]. No reaction was observed for $[Os_3(CO)_{12}]$ under these conditions or when acetonitrile was used as solvent for $[Os_3(CO)_{11}(NCMe)]$, thus we are led to suggest that dissociation and recombination of the labile ligand is involved in the mechanism of formation of clusters (1) and (2) possibly *via* attack of phenyl azide on the intermediate $[Os_3(CO)_{11}]$. Crystals of the products (1) and (2) were deposited by slow evaporation of dichloromethane–hexane solutions at 0 °C under nitrogen.

The structure of $[Os_3(CO)_{10}(CON_3Ph)(NCMe)]$ (1) is shown in Figure 1 and that of $[Os_3(CO)_{10}(CON_3Ph)(NC_5H_5)]$ (2) in Figure 2. Selected bond parameters for the two structures are presented in Table 2. In each complex the Os atoms define a triangle in which one edge is stretched so as to be non-bonding [Os(1) $\cdots$ Os(3) 3.612(2) Å for (1) and 3.615(2) Å for (2)]. The Os(1)–Os(2) and Os(2)–Os(3) distances are longer than the average metal–metal distance of 2.877(3) Å in $[Os_3(CO)_{12}]$.[6] The Os(1)Os(3)N(1)N(2)N(3)C(1)O(1) units are planar and are approximately coplanar with the Os_3 triangles; the phenyl groups co-ordinated to the N(3) atoms of the azide ligands make angles of 101.4° for (1) and 121.1° for (2) with the plane of the azide ligand. The N(1) atom bridges the Os(1) and Os(3) atoms with a slightly shorter bond to the Os(1) atom. The N(1)–N(2) bonds are shorter than the N(2)–N(3) bonds which may indicate that the bonding within the ligand is similar to a resonance hybrid of the type $N{\equiv}\overset{+}{N}{-}\overset{-}{N}R$ in the free ligand. This is in contrast to the symmetric N–N bonds of 1.32(2) Å displayed by the azide ligand in $[Os_3(\mu\text{-}H)(CO)_{10}$-

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† 1,1,1,2,2,2,3,3,3-Decacarbonyl-μ-[1′-oxo-2′-phenyl-2′,3′,4′-triazabut-3′-ene-1′,4′-diyl-C^1(Os^1)$N^{4'}$(Os^1Os^3)]-3-methyl cyanide- and -3-pyridine-triosmium(2*Os*–*Os*).

Supplementary data available (No. SUP 23386, 48 pp.): observed and calculated structure factors, thermal parameters, least-squares planes, hydrogen atom co-ordinates, full bond parameter data. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Spectra data for [$Os_3(CO)_{10}(CON_3Ph)(L)$]

			¹H N.m.r.[a] (in CD_2Cl_2, δ/p.p.m.)		
Compound	L	*m*/*e* ¹⁹²Os	CH_3CN	Aromatic H	ν(CO) [b]/cm⁻¹ (cyclohexane solution)
(1)	$NCCH_3$	1 044	2.64 (3 H, s)	7.48—7.20 (5 H, m)	2 102w, 2 070s, 2 039m, 2 021s, 2 008m, 2 001m, 1 995m, 1 977w, 1 727w,br, 1 663w,br
(2)	NC_5H_5	*c*		8.67—8.60 (2 H, m) 7.98—7.46 (8 H, m)	2 102w, 2 068s, 2 039s, 2 018s, 2 003w, 1 996s, 1 963w, 1 730w,br, 1 698w,br

[a] s = Singlet, m = multiplet. [b] w = Weak, m = medium, s = strong, br = broad. [c] Molecular ion not observed.

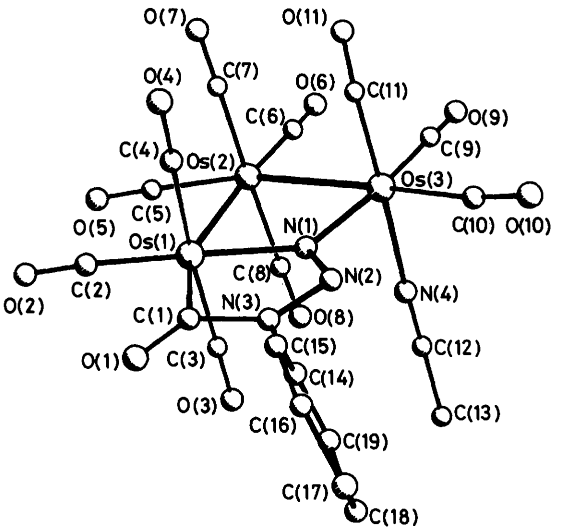

Figure 1. Molecular structure of [$Os_3(CO)_{10}(CON_3Ph)(NCMe)$] (1)

Table 2. Selected bond distances (Å) and angles (°) [$Os_3(CO)_{10}(CON_3Ph)(NCMe)$] (1) and [$Os_3(CO)_{10}(CON_3Ph)(NC_5H_5)$] (2)

	(1)	(2)
Os(1)–Os(2)	2.943(1)	2.936(2)
Os(2)–Os(3)	2.937(1)	2.929(2)
Os(1)–N(1)	2.084(10)	2.041(24)
Os(3)–N(1)	2.128(12)	2.102(20)
Os(1)–C(1)	2.048(17)	1.986(37)
N(1)–N(2)	1.24(2)	1.25(3)
N(2)–N(3)	1.38(2)	1.34(3)
N(3)–C(1)	1.42(2)	1.41(5)
C(1)–O(1)	1.22(2)	1.30(5)
Os(3)–N(4)	2.083(15)	2.140(26)
Os(1)–Os(2)–Os(3)	75.8(1)	76.1(1)
Os(1)–N(1)–Os(3)	121.3(10)	121.5(11)
N(1)–N(2)–N(3)	110.6(11)	114.7(25)
N(2)–N(3)–C(1)	122.1(13)	116.0(25)
Os(1)–C(1)–N(3)	109.0(11)	113.7(24)
Os(1)–C(1)–O(1)	132.5(11)	129.8(29)

Table 3. Crystal data and refinement parameters for [$Os_3(CO)_{10}(CON_3Ph)(NCMe)$] (1) and [$Os_3(CO)_{10}(CON_3Ph)(NC_5H_5)$] (2)

	(1)	(2)
Formula	$C_{19}H_8N_4O_{11}Os_3$	$C_{22}H_{10}N_4O_{11}Os_3\cdot C_6H_{12}$
M	1 038.89	1 161.96
Crystal habit	Rectangular block	Rectangular block
Colour	Yellow	Yellow
Crystal system	Triclinic	Monoclinic
a/Å	9.029(3)	9.311(4)
b/Å	12.720 (5)	16.707(11)
c/Å	13.433(5)	20.241(15)
α/°	102.69(2)	90.0
β/°	102.52(2)	101.88(5)
γ/°	104.75(2)	90.0
U/Å³	1 393.4	3 081.2
D_m	Not measured	Not measured
Z	2	4
D_c/g cm⁻³	2.48	2.50
F(000)	932	2 111
Space group	$P\bar{1}$	$P2_1/n$
λ(Mo-K_α)/Å	0.710 69	0.710 69
μ(Mo-K_α)/cm⁻¹	136.89	123.86
Reflections measured	4 797	4 601
2θ limits/°	$3 < 2\theta < 55°$	$3 < 2\theta < 50°$
Reflections used in refinements	3 739	2 566
[$F > n\sigma(F)$]	$n = 3$	$n = 3$
Weighting scheme	$1/[\sigma^2F + 0.0015F^2]$	$1.6063/[\sigma^2F + 0.0008F^2]$
R	0.057	0.080
$R'[\Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}\|F_o\|]$	0.058	0.074
No. absorption scan data	407	408
Transmission factors min.	0.244	0.420
Transmission factors max.	0.988	0.999

(HN_3H)].[2] The C(1)O(1) carbonyl ligand is involved in the formation of the five-membered ring with the azide group and the Os(1) atom; an uncommon mode of co-ordination for a carbonyl ligand in a metal complex. The Os(1)–C(1) bond length is lengthened with respect to that of a terminal carbonyl group. The two complexes differ in the nature of one of the axial substituent groups on Os(3). In (1) the Os–NCMe distance is similar to the equivalent bond length of 2.074(23) Å in [$Os_3(CO)_{11}(NCMe)$].[7] The Os(3)–N (pyridine) distance in (2) is significantly longer. The carbonyl groups *trans* to the N(4) donor atoms in the two structures show the opposite trend; the Os(3)–C(11) distance in (1) is 1.88(2) Å compared to the value of 1.83(4) Å in (2). This is in keeping with the NCMe exhibiting stronger π-acceptor properties than the NC_5H_5 ligand.

Experimental

Infrared spectra were recorded as solutions in 0.5 mm NaCl cells on a Perkin-Elmer 257 spectrometer with CO calibrant. Mass spectra were obtained using an A.E.1 M.S. 12 instrument at 70 eV ionizing potential. Hydrogen-1 n.m.r. spectra were recorded on a Varian Associates CFT (80 MHz) spectrometer using an internal deuterium lock. Thin layer chromatography

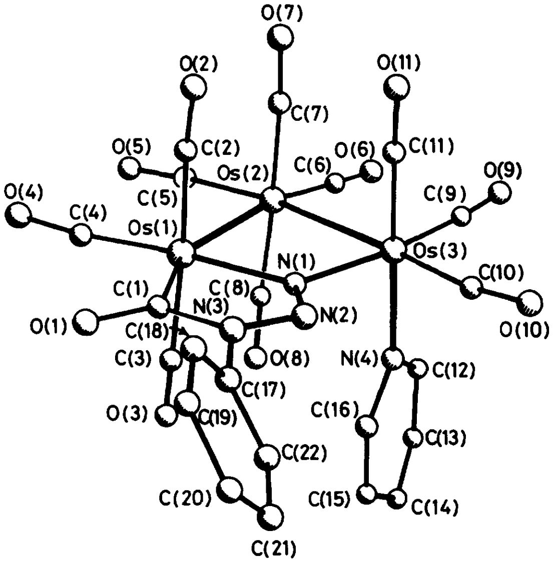

Figure 2. Molecular structure of $[Os_3(CO)_{10}(CON_3Ph)(NC_5H_5)]$ (2)

Table 4. Atom co-ordinates ($\times 10^4$) for compound (1)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Os(1)	452(1)	2 571(1)	1 983(1)
Os(2)	2 309(1)	3 149(1)	518(1)
Os(3)	4 742(1)	3 715(1)	2 568(1)
N(1)	2 709(12)	3 070(9)	3 075(9)
N(2)	2 873(16)	2 984(11)	3 988(10)
N(3)	1 404(15)	2 530(12)	4 135(10)
C(1)	−52(18)	2 231(15)	3 317(11)
O(1)	−1 301(14)	1 813(13)	3 498(9)
C(2)	−1 669(19)	2 112(15)	1 061(13)
O(2)	−2 975(14)	1 784(12)	554(10)
C(3)	599(19)	1 055(14)	1 562(13)
O(3)	687(19)	173(12)	1 355(13)
C(4)	461(19)	4 086(16)	2 499(13)
O(4)	463(18)	5 026(12)	2 847(13)
C(5)	255(17)	2 596(13)	−525(11)
O(5)	−958(14)	2 239(10)	−1 141(9)
C(6)	3 756(19)	3 584(13)	−275(12)
O(6)	4 539(16)	3 802(12)	−831(10)
C(7)	2 032(23)	4 633(14)	912(14)
O(7)	1 852(20)	5 503(12)	1 055(13)
C(8)	2 618(17)	1 685(13)	282(12)
O(8)	2 842(15)	815(11)	71(10)
C(9)	6 311(18)	4 175(13)	1 833(13)
O(9)	7 183(14)	4 413(12)	1 385(11)
C(10)	6 270(21)	4 047(14)	3 944(13)
O(10)	7 218(17)	4 364(13)	4 744(11)
C(11)	4 543(20)	5 177(13)	2 846(12)
O(11)	4 505(17)	6 098(11)	3 076(12)
N(4)	4 858(15)	2 064(11)	2 278(10)
C(12)	4 977(17)	1 200(15)	2 173(11)
C(13)	5 110(27)	42(16)	1 980(17)
C(14)	1 487(19)	2 243(16)	5 129(12)
C(15)	1 112(25)	2 974(17)	5 950(15)
C(16)	1 139(29)	2 635(18)	6 861(25)
C(17)	1 562(28)	1 673(23)	7 000(16)
C(18)	1 820(31)	967(21)	6 231(19)
C(19)	1 827(36)	1 385(21)	5 254(17)
C(100)	5 000	0	5 000

(t.l.c.) was carried out on commercial Merck plates coated with a 0.25 mm layer of silica. Solvents were dried and distilled before use. Phenyl azide,[8] $[Os_3(CO)_{11}(NCMe)]$,[9] and $[Os_3(CO)_{11}(NC_5H_5)]$ [9] were prepared by literature methods.

Table 5. Atom co-ordinates ($\times 10^4$) for compound (2)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Os(1)	5 562(2)	2 156(1)	5 441(1)
Os(2)	3 375(2)	1 803(1)	4 242(1)
Os(3)	4 326(1)	3 429(1)	4 000(1)
N(1)	5 802(24)	3 181(14)	4 912(11)
N(2)	6 664(30)	3 721(17)	5 176(12)
N(3)	7 456(25)	3 543(14)	5 790(13)
C(1)	7 228(41)	2 773(24)	6 038(21)
O(1)	8 025(26)	2 585(15)	6 622(14)
C(2)	4 232(43)	2 621(24)	5 887(21)
O(2)	3 398(31)	2 945(18)	6 134(15)
C(3)	7 277(42)	1 683(23)	5 071(20)
O(3)	8 179(27)	1 471(15)	4 886(13)
C(4)	5 720(45)	1 282(30)	5 982(24)
O(4)	5 592(32)	680(21)	6 304(17)
C(5)	3 161(53)	826(34)	4 617(27)
O(5)	3 159(34)	230(21)	4 896(18)
C(6)	2 169(44)	1 718(25)	3 419(23)
O(6)	1 323(30)	1 602(17)	2 861(15)
C(7)	1 960(46)	2 274(26)	4 671(22)
O(7)	985(29)	2 487(16)	4 928(14)
C(8)	4 961(39)	1 379(22)	3 907(19)
O(8)	5 996(25)	1 134(15)	3 677(12)
C(9)	2 910(40)	3 479(22)	3 246(20)
O(9)	1 935(28)	3 461(15)	2 744(14)
C(10)	5 011(33)	4 427(19)	3 890(16)
O(10)	5 292(25)	5 146(16)	3 832(13)
C(11)	3 013(38)	3 816(22)	4 480(18)
O(11)	2 185(27)	4 106(15)	4 795(13)
N(4)	5 883(25)	2 981(16)	3 449(12)
C(12)	5 539(38)	2 678(21)	2 844(16)
C(13)	6 635(51)	2 347(26)	2 486(19)
C(14)	8 055(43)	2 487(30)	2 733(21)
C(15)	8 448(42)	2 766(30)	3 380(23)
C(16)	7 420(44)	3 053(22)	3 730(18)
C(17)	8 604(33)	4 044(20)	6 132(15)
C(18)	8 654(40)	4 361(20)	6 744(19)
C(19)	9 784(49)	4 835(24)	7 060(16)
C(20)	10 830(66)	5 050(26)	6 725(32)
C(21)	10 782(52)	4 781(35)	6 089(30)
C(22)	9 625(38)	4 250(25)	5 784(20)
C(101) *	4 903(52)	4 733(28)	2 070(18)
C(102) *	4 445(35)	4 009(25)	1 621(21)
C(103) *	5 804(56)	3 567(18)	1 511(24)
C(104) *	6 866(35)	4 161(27)	1 303(25)
C(105) *	6 036(44)	4 930(24)	1 076(18)
C(106) *	5 629(49)	5 337(19)	1 683(27)

* Cyclohexane solvent molecules.

Preparation of $[Os_3(CO)_{10}(CON_3Ph)(L)]$ [L = NCMe (1) *or* NC_5H_5 (2)].—The compound $[Os_3(CO)_{11}(L)]$ (*ca.* 0.100 g) was dissolved in dichloromethane (*ca.* 10 cm^3) and the azide (1.5 equivalents) in dichloromethane (*ca.* 1 cm^3) was introduced. After stirring at 20 °C for 1 h the solvent was removed under vacuum and the residue subjected to t.l.c. (dichloromethane eluant) affording the complexes (1) (44%) and (2) (34%) as intense yellow bands.

Molecular Structure Determinations of $[Os_3(CO)_{10}(CON_3Ph)(NCMe)]$ (1) *and* $[Os_3(CO)_{10}(CON_3Ph)(NC_5H_5)]$ (2).—Crystals of the two complexes were mounted on glass fibres with epoxy-resin adhesive, and unit-cell dimensions and space groups determined *via* Weissenberg (Cu) *X*-ray photography. Intensity data were recorded on a Syntex $P2_1$ diffractometer using graphite-monochromated Mo-K_α radiation and a 96 step $\omega/2\theta$ scan technique. The scan speed varied from 2.0°

min^{-1} to 29.3° min^{-1} depending upon the intensity of the reflection in a 1 s prescan; backgrounds were measured at each end of the scan. Two check reflections were monitored periodically throughout the data collections and showed no significant variations. Accurate cell dimensions for the two complexes were obtained from the centering of 15 strong reflections in the range $15 < 2\theta < 25°$. Details of data collection parameters and the refinements are given in Table 3.

Semi-empirical absorptions and Lorentz polarisation corrections were applied. In the two structures the Os atom positions were located by multisolution Σ_2 sign expansion and the non-hydrogen atoms from subsequent electron-density difference syntheses. The methylene H atoms in (2) were placed in idealised positions (C–H 1.08 Å) and constrained to ride on the relevant C atoms; the H atoms were assigned a common isotropic temperature factor. The refinement of (1) was carried out using blocked-cascade least squares with the Os, N, C, and O atoms assigned anisotropic thermal parameters. A highly disordered solvent molecule was observed in the difference map but the molecule could not be resolved and a single isotropic C atom [C(100)] was placed at the centre of the electron-density for refinement purposes. Structure (2) was refined by blocked full-matrix least squares with the Os, N, and phenyl C atoms assigned anisotropic thermal parameters. A disordered cyclohexane solvent molecule was located in this structure and refined as six isotropic C atoms with C–C distances constrained to be 1.52(1) Å. The refinements were continued until convergence was reached. The atomic fractional co-ordinates for (1) are listed in Table 4 and those for (2) in Table 5.

Complex neutral-atom scattering factors [10] were employed throughout both structure solutions and refinements. All the computations were carried out on the University of Cambridge IBM 370/165 computer using programs written by Professor G. M. Sheldrick. The molecular plots were drawn using the PLUTO package written by Dr. W. D. S. Motherwell.

Acknowledgements

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References

1 K. Burgess, B. F. G. Johnson, J. Lewis, and P. R. Raithby, *J. Organomet. Chem.*, 1982, **224**, C40.
2 B. F. G. Johnson, J. Lewis, P. R. Raithby, and S. W. Sankey, *J. Organomet. Chem.*, 1982, **228**, 135.
3 J. R. Shapley and A. C. Sievert, *J. Am. Chem. Soc.*, 1981, **103**, 6975.
4 R. B. Calvert and J. R. Shapley, *J. Am. Chem. Soc.*, 1977, **99**, 5225; 1978, **100**, 6544, 7726.
5 A. D. Clauss, J. R. Shapley, and S. R. Wilson, *J. Am. Chem. Soc.*, 1981, **103**, 7387.
6 M. R. Churchill and B. G. De Boer, *Inorg. Chem.*, 1977, **16**, 878.
7 P. A. Dawson, B. F. G. Johnson, J. Lewis, J. Puga, P. R. Raithby, and M. J. Rosales, *J. Chem. Soc., Dalton Trans.*, 1982, 233.
8 R. O. Lindsay and C. F. H. Allen, ' Organic Synthesis,' J. Wiley and Sons, London, collective vol. III, p. 710.
9 B. F. G. Johnson, J. Lewis, and D. A. Pippard, *J. Chem. Soc., Dalton Trans.*, 1981, 407.
10 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

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