DALTON

Synthesis and structure of osmium(II) organometallics incorporating a four-membered salicylideneiminium metallacycle and Os–η^1-NO_2 binding

Kausikisankar Pramanik, Prasanta Ghosh and Animesh Chakravorty *

Department of Inorganic Chemistry, Indian Association for the Cultivation of Science,
Calcutta 700 032, India

The reaction of (3-alkyliminio-5-methyl-2-oxidophenyl-*C*^{1},*O*)carbonylbromobis(triphenylphosphine)osmium(II), $[Os(\eta^2\text{-}L^R)(PPh_3)_2(CO)Br]$ **1** (R = Me or Et) with $NaNO_2$ furnished $[Os(\eta^2\text{-}L^R)(PPh_3)_2(CO)(\eta^1\text{-}NO_2)]\cdot H_2O$ **2** (R = Me or Et) in excellent yields. Structure determination of the R = Et complex revealed that the L^R ligand is C,O-chelated and the nitrite is N-bonded with two unequal N–O distances. The oxygen atom of the longer bond is involved in hydrogen bonding with the water molecule. The presence of the hydrogen-bonded iminium phenolato motif in L^{Et} is consistent with ^1H NMR and IR data. The Os–C bond lying *trans* to Os–NO_2 in **2** (R = Et) is lengthened. In going from **1** to **2** a metal-to-ligand charge-transfer band and ν(C≡O) are shifted to higher frequencies and the Os^{III}–Os^{II} reduction potential is shifted anodically. In contrast to **2**, ruthenium affords $[Ru(\eta^1\text{-}L^R)(PPh_3)_2(CO)(\eta^2\text{-}O_2N)]$ in which the nitrite ligand is O,O′-chelated. The origin of this differentiation is scrutinised.

The osmium(II) organometallics $[Os^{II}(\eta^2\text{-}L^R)(PPh_3)_2(CO)Br]$ **1**, incorporating the rare four-membered OsC_2O metallacycle and iminium phenolato hydrogen bonding, were recently isolated in this laboratory *via* decarbonylative metallation of 2,6-diformyl-4-methylphenol by $[Os(PPh_3)_3Br_2]$ in the presence of a primary amine, NRH_2.[1] The ruthenium(II) chloro analogues $[Ru(\eta^2\text{-}L^R)(PPh_3)_2(CO)Cl]$ have also been described[1,2] and replacement of halide by carboxylate has afforded yet other interesting organometallic systems.[3] Herein we explore the feasibility of binding the potentially ambidentate nitrite ion to osmium *via* metathesis of **1**. This endeavour has been motivated by the prospect of realising a rare family since few complexes of NO_2^- with osmium have been structurally characterised[4] and none is an organometallic compound. Further, such a family will provide an opportunity for comparison with the ruthenium counterpart in which nitrite binds only in the O,O′-chelating mode, $[Ru(\eta^1\text{-}L^R)(PPh_3)_2(CO)(\eta^2\text{-}O_2N)]$.[5]

The targeted osmium species have been successfully isolated in the hydrated form, $[Os(\eta^2\text{-}L^R)(PPh_3)_2(CO)(\eta^1\text{-}NO_2)]\cdot H_2O$, and one member has been structurally characterised authenticating the presence of the N-bonded Os–NO_2 motif. Noteworthy features include regiospecific hydrogen bonding, *trans* influence, back bonding and associated effects on bond parameters, spectra and metal redox. The origin of the remarkable ambidentate differentiation between osmium and ruthenium, $Os(\eta^2\text{-}L^R)(\eta^1\text{-}NO_2)$ and $Ru(\eta^1\text{-}L^R)(\eta^2\text{-}O_2N)$, is scrutinised.

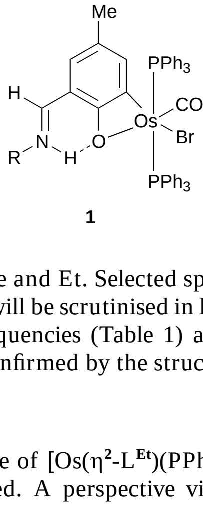
Results and Discussion

Synthesis

The synthetic reaction (1) was carried out by treating compound **1** in a boiling dichloromethane–acetone mixture with an

$$\underset{\mathbf{1}}{[Os(\eta^2\text{-}L^R)(PPh_3)_2(CO)Br]} + NaNO_2 + H_2O \longrightarrow \underset{\mathbf{2}}{[Os(\eta^2\text{-}L^R)(PPh_3)_2(CO)(\eta^1\text{-}NO_2)]\cdot H_2O} + NaBr \quad (1)$$

excess of aqueous $NaNO_2$. The diamagnetic (Os^{II}, t_2^6) non-electrolytic complex **2** is afforded in excellent yield as a light orange crystalline material. The relevant R substituents in the present work are Me and Et. Selected spectral data are listed in Tables 1 and 2 and will be scrutinised in later sections. The three NO_2^- vibration frequencies (Table 1) are consistent[6] with N-bonding which is confirmed by the structure determination.



1

Structure

The crystal structure of $[Os(\eta^2\text{-}L^{Et})(PPh_3)_2(CO)(\eta^1\text{-}NO_2)]\cdot H_2O$ has been determined. A perspective view of the molecule is shown in Fig. 1 and selected bond parameters are listed in Table 3. Nitrite binding occurs *via* the nitrogen atom, the L^{Et} ligand being chelated to the metal at the aromatic carbon C(37) and the phenolato oxygen O(1). The distorted octahedral coordination sphere of the metal is completed by two PPh_3 ligands in *trans* dispositions and the carbon monoxide molecule. Only one other nitrite complex of osmium(II), $[Os(NO)(NO_2)_4(OH)]^{2-}$, appears to have been structurally characterised.[4] The present complex and its bromo analogue also represent the only known structures incorporating Os^{II}–O (phenolato) binding and a four-membered OsC_2O metallacycle. Structurally characterised orthometallated osmium(II) species are generally rare.[7]

The $OsNO_2$ motif is highly planar (mean deviation 0.005 Å) and makes a dihedral angle of 14.2° with the OsL^{Et} plane, see below. The strong *trans* influence[8] of the N-bonded NO_2^- is reflected in a substantially longer Os–C(37) bond, 2.137(14) Å, compared to 1.980(19) Å in $[Os(\eta^2\text{-}L^{Et})(PPh_3)_2(CO)Br]$.[1] The water molecule O(5) occupies a region such that it can hydrogen bond strongly with nitro O(4) as well as weakly with the phenolato oxygen O(1) and iminium nitrogen N(1), the O(5)···O(4), O(5)···O(1) and O(5)···N(1) distances being 2.834(20), 3.078(25) and 3.039(25) Å respectively. The nitro

Table 1 Electronic and IR spectral and electrochemical data

	UV/VIS[a]	IR[b]/cm^{-1}						Reduction potential[c]
		NO$_2^-$						
Compound	λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})	ν_{asym}	ν_{sym}	δ	C≡O	H$_2$O[d]	C≡N	$E_{\frac{1}{2}}$/V (ΔE_p/mV)
[Os(η^2-L^{Et})(PPh$_3$)$_2$(CO)(η^1-NO$_2$)]·H$_2$O	475 (2990), 335 (4480)	1330vs	1280vs	840m	1880vs	3400br	1630vs	0.63 (170)
[Os(η^2-L^{Me})(PPh$_3$)$_2$(CO)(η^1-NO$_2$)]·H$_2$O	475 (3090), 335 (4590)	1330vs	1275vs	840m	1890vs	3400br	1640vs	0.66 (120)

[a] Solvent is dichloromethane. [b] In KBr disc unless otherwise stated: v = very, s = strong, m = medium, br = broad. [c] Solvent, dichloromethane; supporting electrolyte, NEt$_4$ClO$_4$ (0.1 mol dm^{-3}); working electrode, platinum; reference electrode, SCE; solute concentration, ≈10^{-3} mol dm^{-3}; $E_{\frac{1}{2}} = 0.5(E_{pa} + E_{pc})$ at scan rate 50 mV s^{-1}, where E_{pa} and E_{pc} are the anodic and cathodic peak potentials respectively; $\Delta E_p = E_{pa} - E_{pc}$. [d] In hexachlorobutadiene.

Table 2 Proton NMR data in CDCl$_3$*

	δ(J/Hz)					
Compound	H^{42}	H^{40}	H^{44}	NH$^+$	Me^{41}	NEt/NMe
[Os(η^2-L^{Et})(PPh$_3$)$_2$(CO)(η^1-NO$_2$)]·H$_2$O	5.64 (s)	6.68 (s)	6.84 (s)	11.2 (s)	1.81 (s)	3.21 (q, 8.5) 1.22 (t, 8.5)
[Os(η^2-L^{Me})(PPh$_3$)$_2$(CO)(η^1-NO$_2$)]·H$_2$O	5.64 (s)	6.70 (s)	6.80 (s)	11.2 (s)	1.86 (s)	2.90 (s)

* Atom numbering is as in Fig. 1; SiMe$_4$ as internal standard; s = singlet, q = quartet, t = triplet.

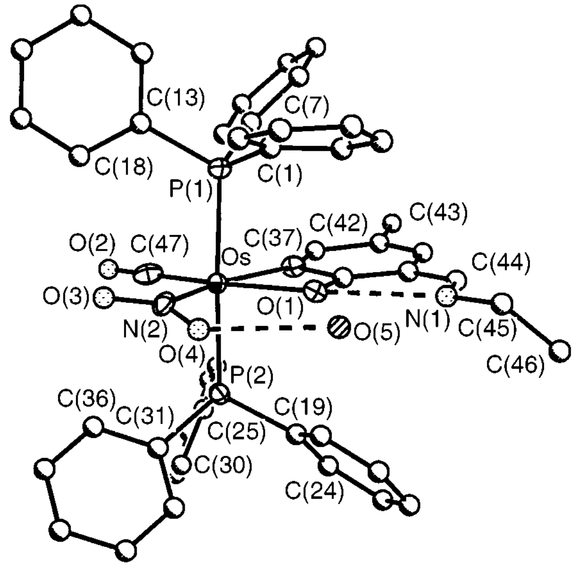


Fig. 1 Perspective view and atom-labelling scheme for [Os(η^2-L^{Et})(PPh$_3$)$_2$(CO)(η^1-NO$_2$)]·H$_2$O

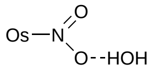
group is unsymmetrical, N(2)–O(3) 1.188(16) and N(2)–O(4) 1.267(18) Å reflecting the importance of the hydrogen-bonded canonical form **3**. Water binding of this type is unusual among structurally characterised complexes having the M^{II}–NO$_2$ motif (M = Ru or Os).[4,9]

The four-membered L^{Et} chelate ring is nearly perfectly planar (mean deviation 0.004 Å) and indeed the entire L^{Et} fragment excluding the Me and Et groups is an excellent plane (mean deviation 0.03 Å) with which the carbon monoxide molecule is virtually coplanar. The Os–C(37) bond is longer by 0.29 Å than the Os–C(47) bond. The size trend C(sp^2) > C(sp), Os^{II}–CO back bonding and the *trans* influence of η^1-NO$_2$ are the contributing factors. The P(1)–Os–P(2) axis is approximately perpendicular to the above-noted L^{Et} plane ensuring that none of the PPh$_3$ phenyl rings approaches the plane too closely.

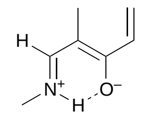
The Os–O(1) length, 2.181(10) Å, is comparable to that, 2.151(10) Å, in the bromo analogue.[1] No other Os^{II}–O (phenolato) lengths are available for comparison. The average Os^{III}–O length in a catechol complex is 2.07 Å.[10] The N(1)···O(1) length, 2.729(20) Å, taken collectively with spectral data (see below) is consistent with the presence of the hydrogen-bonded iminium phenolato zwitterionic motif **4**.

Table 3 Selected bond distances (Å) and angles (°) for [Os(η^2-L^{Et})(PPh$_3$)$_2$(CO)(η^1-NO$_2$)]·H$_2$O

Os–P(1)	2.381(4)	Os–P(2)	2.367(4)
Os–O(1)	2.181(10)	Os–N(2)	2.135(11)
Os–C(37)	2.137(14)	Os–C(47)	1.849(15)
O(2)–C(47)	1.142(20)	N(1)–C(44)	1.316(24)
O(3)–N(2)	1.188(16)	O(4)–N(2)	1.267(18)
O(1)···N(1)	2.729(20)	O(5)···O(4)	2.834(20)
P(1)–Os–P(2)	177.4(1)	P(1)–Os–O(1)	87.9(3)
P(2)–Os–O(1)	89.9(3)	P(1)–Os–N(2)	91.1(4)
P(2)–Os–N(2)	90.4(4)	O(1)–Os–N(2)	94.5(4)
P(1)–Os–C(37)	87.0(4)	P(2)–Os–C(37)	90.9(4)
O(1)–Os–C(37)	64.8(5)	N(2)–Os–C(37)	159.2(5)
P(1)–Os–C(47)	92.6(5)	P(2)–Os–C(47)	89.3(5)
O(1)–Os–C(47)	167.0(5)	N(2)–Os–C(47)	98.5(6)
C(37)–Os–C(47)	102.2(6)	Os–C(47)–O(2)	178.0(13)
Os–N(2)–O(3)	129.1(10)	Os–N(2)–O(4)	116.6(9)
O(3)–N(2)–O(4)	114.3(12)		



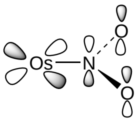
3



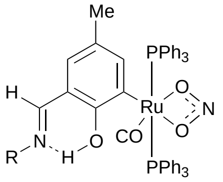
4

NMR and IR spectra

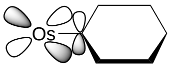
Both ^{1}H NMR and IR data of compound **2** are consistent with the presence of motif **4**. The N–H stretch is expected[1,2] near 3400 cm^{-1} but it could not be resolved from the broad and intense water band in the same region (Table 1). The N–H proton is however observed as a broad resonance in ^{1}H NMR at δ 11.2, the signal disappearing upon shaking with D$_2$O. The relatively high C=N stretching frequency (≈1640 cm^{-1}, Table 1) is also consistent with the iminium description.[11,12] Further, the aldimine CH proton in free Schiff bases of 2,6-diformyl-4-methylphenol resonates near δ 8.7. The corresponding resonance for the present complexes occurs near δ 6.8 (H^{44}, Table 2). Upon protonation of the imine nitrogen, as in motif **4**, a significant high-field shift of the aldimine CH signal is indeed anticipated.[13] The hydrogen bonding in motif **4** has some features similar to those in rhodopsin chemistry.[11]



5



6



7

The aromatic H^{40} and H^{42} as well as the Me^{41} singlets occur at relatively high fields in the ^1H NMR spectra (Table 2). From the X-ray structural work, these protons are indeed found to lie well within the shielding cones of phosphine phenyl rings. For the conformation in the crystal, the extent of shift computed from crystallographic data and isoshielding ρ *vs.* *z* plots[14] are: H^{40}, 0.55; H^{42}, 0.75 and Me^{41}, 0.62 ppm.[15]

Charge-transfer spectra and metal redox

Two characteristic allowed electronic bands of compound **2** occur at 475 and 335 nm (Table 1). The first, assigned to a $t_2 \longrightarrow \pi^*(L)$ metal-to-ligand charge-transfer (MLCT) excitation, is blue shifted with respect to the corresponding band of the bromo precursor (500 nm). In effect the t_2 shell lies lower in the nitro complex. One plausible reason is the superior π-accepting power of the nitro group leading to d_π–p_{π^*} Os–NO_2 back bonding, schematically depicted in **5**. Significantly, the C≡O stretching frequency of **2** (Table 1) is ≈30 cm^{-1} higher than that of **1**.

The type **2** complexes display a quasi-reversible one-electron cyclic voltammetric response in dichloromethane solution corresponding to osmium(III)–osmium(II) redox. The reduction potentials (Table 1) lie near 0.65 V *vs.* saturated calomel electrode (SCE). For the bromo precursor the potential is lower, ≈0.50 V. This is consistent with the higher stability of the electroactive t_2 shell in **2**.

The osmium–ruthenium contrast

Unlike $[Os(\eta^2\text{-}L^R)(PPh_3)_2(CO)Br]$ the ruthenium complex $[Ru(\eta^2\text{-}L^R)(PPh_3)_2(CO)Cl]$ reacts with $NaNO_2$ affording **6** in which nitrite is O,O′-chelated and the L^R ligand is monohapto [no Ru–O (phenolato) bond].[5] The covalent radii of ruthenium(II) and osmium(II) are virtually equal,[16] yet the M–O and M–C lengths in the $M(\eta^2\text{-}L^R)$ fragment in $[Os(\eta^2\text{-}L^R)(PPh_3)_2(CO)Br]$ are shorter than those in $[Ru(\eta^2\text{-}L^R)(PPh_3)_2(CO)Cl]$ by ≈0.1 Å. The metallated ring is thus pulled closer to osmium. This can arise from the stronger d_π–p_{π^*} back bonding[17] in the case of osmium as depicted in **7**. In **7** the aromatic π^* orbital corresponds to an idealised e_2 orbital of benzene.[18] The stronger $Os(\eta^2\text{-}L^R)$ binding is believed to be a major reason for retention of the chelate mode of L^R in going from **1** to **2**. The required six-co-ordination of the metal ensures that nitrite is bonded in the monohapto fashion and softness trends ($Os^{II} > Ru^{II}$ and $N^{-III} > O^{-II}$) favour Os–NO_2 bonding. In the case of $[Ru(\eta^2\text{-}L^R)(PPh_3)_2(CO)Cl]$ the weaker $Ru(\eta^2\text{-}L^R)$ chelation is superseded by nitrite chelation affording **6**.

Conclusion

A pair of metallacycles of type $[Os(\eta^2\text{-}L^R)(PPh_3)_2(CO)(\eta^1\text{-}NO_2)]\cdot H_2O$ **2**, incorporating rare instances of N (nitro), O (phenolato) and C (aryl) binding to osmium(II) as well as of nitro–water and iminium–phenolato hydrogen bonding, have been synthesized. The ambidentate differentiation between the two metals expressed in the motifs $Os(\eta^2\text{-}L^R)(\eta^1\text{-}NO_2)$ and $Ru(\eta^1\text{-}L^R)(\eta^2\text{-}O_2N)$ is attributed to the superior back-bonding ability and softness of bivalent osmium.

Experimental

Materials

The starting materials $[Os(PPh_3)_3Br_2]$[19] and 2,6-diformyl-4-methylphenol[20] were synthesized by the reported procedures. The bromo complexes $[Os(\eta^2\text{-}L^R)(PPh_3)_2(CO)Br]$ were prepared by the methods described earlier.[1] The purification of dichloromethane and the preparation of tetraethylammonium perchlorate for electrochemical/spectroscopic work were as before.[21] Sodium nitrite and other chemicals and solvents were of analytical grade used without further purification.

Physical measurements

The UV/VIS spectra were recorded on a Hitachi 330 spectrophotometer and IR (4000–200 cm^{-1}) spectra (as KBr discs) on a Perkin-Elmer 783 spectrophotometer. A Bruker 270 MHz FT spectrometer was used to obtain ^1H NMR data (tetramethylsilane is the internal standard). Microanalyses (C, H, N) were carried out with a Perkin-Elmer 240C elemental analyser. Electrochemical measurements were performed under a nitrogen atmosphere with PAR 370-4 electrochemistry apparatus.[21] All the reported potentials in this work are uncorrected for junction contribution. Solution electrical conductivities were examined using a Philips PR9500 bridge.

Preparation of complexes

The $[Os(\eta^2\text{-}L^R)(PPh_3)_2(CO)(\eta^1\text{-}NO_2)]\cdot H_2O$ complexes were obtained in 85–90% yields by treating $[Os(\eta^2\text{-}L^R)(PPh_3)_2(CO)Br]$ with $NaNO_2$. Details are given below for R = Et.

Carbonyl(3-ethyliminio-5-methyl-2-oxidophenyl-*C*^{1},*O*)nitrobis(triphenylphosphine)osmium(II) monohydrate, $[Os(\eta^2\text{-}L^{Et})(PPh_3)_2(CO)(\eta^1\text{-}NO_2)]\cdot H_2O$. To a solution of $[Os(\eta^2\text{-}L^{Et})(PPh_3)_2(CO)Br]$ (50 mg, 0.05 mmol) in dichloromethane–acetone (1:1, 40 cm^3) was added an aqueous solution of an excess of $NaNO_2$ (50 mg). The mixture was heated to reflux for 2.5 h and the original dark red solution turned light orange. Organic solvents were then removed under reduced pressure and the resulting aqueous suspension of the required compound was filtered off, washed repeatedly with water and dried *in vacuo* (Found: C, 58.1; H, 4.7; N, 2.8. $C_{47}H_{44}N_2O_5OsP_2$ requires C, 58.3; H, 4.6; N, 2.9%).

The complex $[Os(\eta^2\text{-}L^{Me})(PPh_3)_2(CO)(\eta^1\text{-}NO_2)]\cdot H_2O$ was similarly prepared (Found: C, 57.7; H, 4.3; N, 3.0. $C_{46}H_{42}N_2O_5OsP_2$ requires C, 57.9; H, 4.4; N, 2.9%).

Crystallography

A single crystal of $[Os(\eta^2\text{-}L^{Et})(PPh_3)_2(CO)(\eta^1\text{-}NO_2)]\cdot H_2O$ (0.22 × 0.16 × 0.24 mm) grown by slow diffusion of hexane into dichloromethane solution was mounted. Cell parameters were determined by least-squares fit of 30 machine-centred reflections (rotation photo). Data were successfully collected by the ω-scan technique in the range $2 \leqslant 2\theta \leqslant 50°$ on a Siemens R3m/V four-circle diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\,73$ Å). The intensities of the two check reflections measured after every 98 did not change significantly in the course of data collection. Data were corrected for Lorentz-polarisation effects and an empirical absorption correction was done on the basis of azimuthal scans of six reflections.[22] Total collected reflections were 10 572, of which

Table 4 Crystallographic data for $[Os(\eta^2\text{-}L^{Et})(PPh_3)_2(CO)(\eta^1\text{-}NO_2)]\cdot H_2O$

Formula	$C_{47}H_{44}N_2O_5OsP_2$
M	969.0
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	10.534(2)
b/Å	20.613(8)
c/Å	19.300(6)
β/°	96.87(2)
U/Å^3	4161(2)
Z	4
T/°C	22
D_c/g cm^{-3}	1.547
μ/cm^{-1}	3.190
Transmission coefficients	0.2330–0.3878
R^a	0.0536
R'^b	0.0577
Goodness of fit	1.19

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$; $w^{-1} = \sigma^2(|F_o|) + g|F_o|^2$, $g = 0.0005$.

7359 were unique and 3457 were used as observed $[I > 3\sigma(I)]$ for structure solution and refinements. Systematic absences led to the space group $P2_1/n$. The osmium atom was located from Patterson maps and the other non-hydrogen atoms emerged from successive Fourier synthesis. All the non-hydrogen atoms except water oxygen were refined anisotropically and hydrogen atoms were added at calculated positions with fixed $U = 0.08$ Å^2. Refinement was carried out by full-matrix least-squares procedures. The highest residual was 0.90 e Å^{-3} close to the metal atom. All calculations were done on a MicroVax II computer using the SHELXTL PLUS program package.[23] Significant crystal data are listed in Table 4.

CCDC reference number 186/632.

Computation of chemical shifts due to PPh_3 ring currents

The crystallographic data of $[Os(\eta^2\text{-}L^{Et})(PPh_3)_2(CO)(\eta^1\text{-}NO_2)]\cdot H_2O$ were used. The cylindrical coordinates (ρ and z)[24] of the protons with respect to the centroids (G) of the PPh_3 phenyl rings were determined from (*i*) the distance of the proton from the centroid (G) of each PPh_3 phenyl ring and (*ii*) the angle between the distance vector and the normal to the plane of the ring at G. These calculated ρ and z values were expressed in units of the radius of the benzene hexagon and the shifts were estimated with the help of the available isoshielding ρ *vs.* z plots.[14] The net shift of a proton was obtained by summing the individual contributions from all the rings.

Acknowledgements

We thank the Department of Science and Technology, Council of Scientific and Industrial Research and the Indian National Science Academy, New Delhi for financial support. Affiliation to Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, India is acknowledged.

References

1 P. Ghosh, N. Bag and A. Chakravorty, *Organometallics*, 1996, **15**, 3042.
2 N. Bag, S. B. Choudhury, A. Pramanik, G. K. Lahiri and A. Chakravorty, *Inorg. Chem.*, 1990, **29**, 5013; N. Bag, S. B. Choudhury, G. K. Lahiri and A. Chakravorty, *J. Chem. Soc., Chem. Commun.*, 1990, 1626.
3 P. Ghosh, A. Pramanik and A. Chakravorty, *Organometallics*, 1996, **15**, 4147.
4 A. S. Salomov, N. A. Parpiev, K. T. Sharipov, V. N. Kokunova, N. M. Sinitsyn and M. A. Porai-Koshits, *Russ. J. Inorg. Chem.*, 1984, **29**, 1633.
5 P. Ghosh and A. Chakravorty, *Inorg. Chem.*, 1997, **36**, 64.
6 M. A. Hitchman and G. L. Rowbottom, *Coord. Chem. Rev.*, 1982, **42**, 55; K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th edn., Wiley, New York, 1986.
7 Z. Dawodi, M. J. Mays and P. R. Raithby, *Acta Crystallogr., Sect. B*, 1981, **37**, 252.
8 J. E. Huheey, E. A. Keiter and R. L. Keiter, *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th edn., Harper Collins College Publishers, New York, 1993.
9 R. A. Leising, S. A. Kubow, M. R. Churchill, L. A. Buttrey, J. W. Ziller and K. J. Takeuchi, *Inorg. Chem.*, 1990, **29**, 1306; A. J. Blake, R. O. Gould, B. F. G. Johnson and E. Parisini, *Acta Crystallogr., Sect. C*, 1992, **48**, 982; M. A. A. F. de C. T. Carrondo, P. R. Rudolf, A. C. Skapski, J. R. Thornback and G. Wilkinson, *Inorg. Chim. Acta*, 1977, **24**, L95; D. Ooyama, N. Nagao, H. Nagao, Y. Miura, A. Hasegawa, K.-I. Ando, F. S. Howell, M. Mukaida and K. Tanaka, *Inorg. Chem.*, 1995, **34**, 6024.
10 M. Haga, K. Isobe, S. R. Boone and C. G. Pierpont, *Inorg. Chem.*, 1990, **29**, 3795.
11 C. Sandorfy and D. Vocelle, *Molecules in Physics, Chemistry and Biology*, Kluwer, 1989, vol. 4, p. 195.
12 H. Bohme and M. Haake, *Advances in Organic Chemistry*, eds. H. Bohme and H. G. Viehe, Interscience, New York, 1976, part 1, vol. 9, p. 1.
13 G. M. Sharma and O. A. Roels, *J. Org. Chem.*, 1973, **38**, 3648.
14 C. E. Johnson, jun. and F. A. Bovey, *J. Chem. Phys.*, 1958, **29**, 1012.
15 P. Ghosh, Ph.D. Thesis, Jadavpur University, Calcutta, 1995.
16 L. Pauling, *The Nature of the Chemical Bond and the Structure of Molecules and Crystals*, 3rd edn., Cornell University Press, Ithaca, NY, 1960.
17 T. Hasegawa, M. Sekine, W. P. Schaefer and H. Taube, *Inorg. Chem.*, 1991, **30**, 449; H. Taube, *Pure Appl. Chem.*, 1991, **63**, 651; W. D. Herman and H. Taube, *J. Am. Chem. Soc.*, 1987, **109**, 8101; H. Taube, *Pure Appl. Chem.*, 1979, **51**, 901.
18 F. A. Cotton, *Chemical Applications of Group Theory*, Wiley Eastern Limited, New Delhi, 1971.
19 P. R. Hoffman and K. G. Caulton, *J. Am. Chem. Soc.*, 1975, **99**, 4221.
20 F. Ullman and K. Brittner, *Chem. Ber.*, 1909, **42**, 2539; R. R. Gagne, C. L. Spiro, T. J. Smith, C. A. Hamann, T. Thies and A. K. Shiemke, *J. Am. Chem. Soc.*, 1981, **103**, 4073.
21 P. Ghosh, A. Pramanik, N. Bag, G. K. Lahiri and A. Chakravorty, *J. Organomet. Chem.*, 1993, **454**, 237.
22 A. C. T. North, D. C. Phillips and F. A. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.
23 G. M. Sheldrick, SHELTXTL PLUS, Structure Determination Software Programs, Siemens Analytical X-Ray Instruments, Madison, WI, 1990.
24 H. Margenau and G. M. Murphy, *The Mathematics of Physics and Chemistry*, D. Van Nostrand, Princeton, NJ, 1956.

Received 25*th March* 1997; *Paper* 7/02070H