Journal of Organometallic Chemistry, 216 (1981) 255—262
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

MIGRATORY-INSERTION REACTIONS OF OSMIUM(II) ETHYL COMPLEXES DERIVED FROM AN OSMIUM(0) ETHYLENE COMPLEX

K.R. GRUNDY and W.R. ROPER *

Department of Chemistry, University of Auckland, Auckland (New Zealand)

(Received February 6th, 1981)

Summary

Reaction between $Os(CO)_2(PPh_3)_3$ and C_2H_4 gives $Os(\eta^2\text{-}C_2H_4)(CO)_2(PPh_3)_2$. A series of osmium(II) ethyl complexes, $OsEtX(CO)_2(PPh_3)_2$ (X = Cl, I, O_2CCF_3, $OClO_3$) results from reaction of $Os(\eta^2\text{-}C_2H_4)(CO)_2(PPh_3)_2$ with one equivalent of the appropriate acid. In the presence of excess HCl a migratory-insertion reaction ensues and the resulting propionyl ligand is protonated on oxygen to give an hydroxy-carbene complex $OsCl_2[C(OH)Et](CO)(PPh_3)_2$. Migration of the ethyl group in $OsEt(OClO_3)(CO)_2(PPh_3)_2$ is induced by addition of CO, CNR or the potentially bidentate ligand $S_2CNEt_2^-$ giving $[Os[C(O)Et](CO)_3(PPh_3)_2]ClO_4$, $[Os[C(O)Et](CO)(CNR)_2(PPh_3)_2]ClO_4$ and $Os[C(O)Et](S_2CNEt_2)(CO)(PPh_3)_2$, respectively.

Introduction

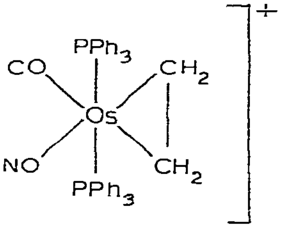
Osmium compounds of the type $OsRX(CO)_2(PPh_3)_2$ where R = *p*-tolyl [1] and methyl [2] have been recently described and, in striking contrast with the analogous ruthenium compounds [1,3], have been found resistant to migratory-insertion reactions. There is theoretical evidence [4] suggesting a trend towards greater ease of migration with increasing hydrocarbon chain length and it was therefore of some interest to study the compounds $OsRX(CO)_2(PPh_3)_2$ for R = Et. In fact, insertion reactions involving the osmium—ethyl bond are already known in that $OsEt_2(CO)_4$ is converted to $Os[C(O)Et]_2(CO)_4$ under CO pressure [5]. Since $Os(\eta^2\text{-}C_2H_4)(CO)_2(PPh_3)_2$ was available to us [6], we have made use of this in the synthesis of a series of compounds $OsEtX(CO)_2(PPh_3)_2$ and we describe here the characterisation of these compounds and the migratory-insertion reactions which they undergo.

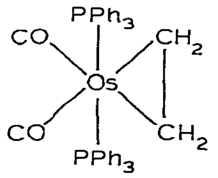
0022-328X/81/0000—0000/$ 02.50, © 1981, Elsevier Sequoia S.A.

Results and discussion

When subjected to ethylene (1 atm) and pyrex-filtered, full sunlight or a tungsten-halogen lamp, a yellow benzene solution of $Os(CO)_2(PPh_3)_3$ is decolourised within minutes. The addition of ethanol produced a white crystalline precipitate of $Os(\eta^2\text{-}C_2H_4)(CO)_2(PPh_3)_2$. In the absence of light, this reaction is considerably slower and it is likely that the photolytic enhancement of rate is due to rapid dissociation of a phosphine ligand from electronically excited $Os(CO)_2(PPh_3)_3$.

The ethylene adduct, $Os(\eta^2\text{-}C_2H_4)(CO)_2(PPh_3)_2$, has been characterised by elemental analysis, ^1H NMR and IR spectroscopy. The ^1H NMR spectrum ($CDCl_3$) exhibits a triplet due to coordinated ethylene at τ 9.55, establishing the presence of equivalent phosphine ligands ($^3J(H\text{—}P) = 7$ Hz). The ^1H NMR spectrum of the isoelectronic cation $[Os(\eta^2\text{-}C_2H_4)(CO)(NO)(PPh_3)_2]^+$ [7] at room temperature similarly displays a triplet at τ 7.38 ($^3J(H\text{—}P) = 5.3$ Hz). The decreased shielding in this complex can be attributed to the positive charge. The low temperature ^{13}C NMR spectrum of $[Os(\eta^2\text{-}C_2H_4)(CO)(NO)(PPh_3)_2]^+$ consists of two well separated resonances due to the ethylene carbon atoms, thus indicating an unsymmetrical environment for the ethylene ligand and in conjunction with the triplet in the ^1H NMR a pseudo-octahedral geometry is indicated.





The IR spectrum of $Os(\eta^2\text{-}C_2H_4)(CO)_2(PPh_3)_2$ shows two strong absorptions of equal intensity at 1955 and 1895 cm^{-1}, indicative of *cis* carbonyl groups. On this basis, and by analogy with the nitrosyl compound, $Os(\eta^2\text{-}C_2H_4)(CO)_2(PPh_3)_2$ can also be assigned octahedral geometry.

When the ^1H NMR spectrum of $Os(\eta^2\text{-}C_2H_4)(CO)_2(PPh_3)_2$ was run under an atmosphere of ethylene the signal due to coordinated ethylene was unchanged and a sharp singlet at τ 4.60 appeared due to free ethylene. Thus, if exchange is occurring then the rate is fairly slow. Observations on the chemistry of $Os(\eta^2\text{-}C_2H_4)(CO)_2(PPh_3)_2$ would suggest that slow exchange is likely to occur and that the coordinated ethylene is relatively labile as is evidenced by the regeneration of $Os(CO)_2(PPh_3)_3$ when the ethylene complex is heated in benzene with triphenylphosphine.

The compounds $[Os(\eta^2\text{-}C_2H_4)(CO)(NO)(PPh_3)_2]^+$ and $Os(\eta^2\text{-}C_2H_4)(CO)_2(PPh_3)_2$ appear to be the only ethylene complexes of osmium. Other olefin complexes are known, but in these the ligands involved are chelating oligo-olefins or olefins with electron-withdrawing substituents. Although electrophilic addition to chelating oligo-olefins is a widely observed phenomenon, examples of addition to mono-olefins are comparatively rare and largely restricted to fluoro-olefins. Various rhodium(I) fluoro-olefin complexes react with hydrogen chlo-

TABLE 1

IR DATA [a] FOR $Os(\eta^2\text{-}C_2H_4(CO)_2(PPh_3)_2$ AND DERIVATIVES

Compound	ν(CO) (cm^{-1})	Other bands (cm^{-1})
$Os(\eta^2\text{-}C_2H_4)(CO)_2(PPh_3)_2$	1955, 1895	
$OsEtCl(CO)_2(PPh_3)_2$	2015, 1945	
$OsEtI(CO)_2(PPh_3)_2$	2010, 1945	
$OsEt(O_2CCF_3)(CO)_2(PPh_3)_2$	2030, 1950	1680, 1190 (CF_3CO_2)
$OsEt(OClO_3)(CO)_2(PPh_3)_2$	2030, 1950	1110, 1060 ($OClO_3$)
$OsCl_2[C(OH)Et](CO)(PPh_3)_2$	1935	3500w ν(OH) 160w δ(OH)
$[Os[C(O)Et](CO)_3(PPh_3)_2]ClO_4$	2140w, 2060, 2040	1610s ν(C=O)
$[Os[C(O)Et](CO)(CNR)_2(PPh_3)_2]ClO_4$	1990	2190w, 2150, ν(CN) 1590s ν(C=O)
$Os[C(O)Et](S_2CNEt_2)(CO)(PPh_3)_2$	1940, 1930, 1905	1540m ν(C=O)

[a] Measured as Nujol mulls. All bands strong or very strong, unless noted otherwise.

ride to give fluoroethyl derivatives [8], e.g.:

$$Rh(\eta^2\text{-}C_2F_4)ClL_2 + HCl \rightarrow Rh(CF_2CF_2H)Cl_2L_2$$

Fluoro-olefin complexes of platinum(0) react similarly with trifluoroacetic acid [9]:

$$Pt(\eta^2\text{-}C_2F_3X)L_2 + CF_3CO_2H \rightarrow Pt(CFXCF_2H)(O_2CCF_3)L_2$$

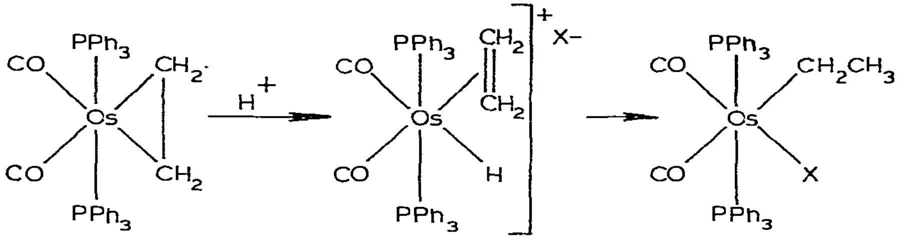
($X = CF_3$, Cl, Br, H).

In solution, $Os(\eta^2\text{-}C_2H_4)(CO)_2(PPh_3)_2$ reacts with one equivalent of the acids HX ($X = Cl, I, O_2CCF_3, OClO_3$) to give white crystalline *cis*-$OsEtX(CO)_2(PPh_3)_2$. This formulation was verified by elemental analysis, IR and ^1H NMR spectroscopy. Values of ν(CO) (see Table 1) are low for typical $OsX_2(CO)_2(PPh_3)_2$ complexes, indicating the presence of a strongly σ-donating anionic ligand. There are no characteristic IR absorptions attributable to the ethyl group, although several weak bands in the 1400—800 cm^{-1} region may arise from this ligand. The ^1H NMR spectrum ($CDCl_3$) shows a complex multiplet (5H) with the maximum intensity signal occurring at ca. τ 9.0.

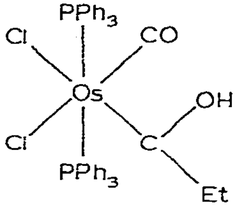
An example of the addition of a protic acid to coordinated ethylene is the following case where ^1H NMR evidence was obtained for the addition of hydrogen chloride to $Rh(\eta^2\text{-}C_2H_4)_2(\eta^5\text{-}C_5H_5)$ [10]:

$$Rh(\eta^2\text{-}C_2H_4)_2(\eta^5\text{-}C_5H_5) + HCl \rightarrow RhEtCl(\eta^2\text{-}C_2H_4)(\eta^5\text{-}C_5H_5)$$

These ethyl complexes may be formed either through protonation at the metal followed by hydride transfer to coordinated ethylene, or by direct protonation at the ethylene ligand.

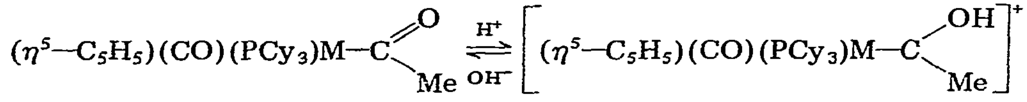


The reaction of $Os(\eta^2\text{-}C_2H_4)(CO)_2(PPh_3)_2$ with an excess of hydrochloric acid proceeds quite differently from the reactions described above. The white crystalline solid isolated has stoichiometry $Os(\eta^2\text{-}C_2H_4)(CO)_2(PPh_3)_2 \cdot 2\,HCl$, and has been formulated as an ethylhydroxycarbene complex, $OsCl_2[C(OH)Et](CO)(PPh_3)_2$. The IR spectrum exhibits one strong $\nu(CO)$ at 1935 cm^{-1} with other maxima at 3500m $\nu(OH)$, 1610w $\delta(OH)$, 1400m, 1310m, 1289m, 1265s $\nu(CO)$, 1070m, 975w, 920m, 890m, 860w, 850w, and 785 cm^{-1}. The ^1H NMR spectrum displays signals attributable to triphenylphosphine protons and an ethyl group τ 8.2, q, 2 H; 9.9, t, 3 H). Thus $OsCl_2[C(OH)Et](CO)(PPh_3)_2$ is assigned the structure



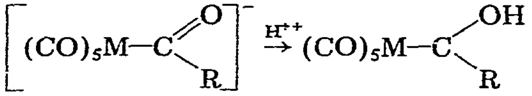
Recrystallisation in the presence of strong base gives $OsEtCl(CO)_2(PPh_3)_2$ and further recrystallisation of this in the presence of hydrochloric acid regenerates $OsCl_2[C(OH)Et](CO)(PPh_3)_2$ (see Scheme 1).

Hydroxycarbene complexes have been previously characterised. Protonation of the acetyl ligand in $M(COMe)(CO)(PCy_3)(\eta^5\text{-}C_5H_5)$ (M = Fe, Ru) yielded cationic methylhydroxycarbene complexes [11]:



$$(\eta^5\text{—}C_5H_5)(CO)(PCy_3)M\text{—}C\begin{matrix}\nearrow\!\!O\\ \searrow Me\end{matrix} \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} \left[(\eta^5\text{—}C_5H_5)(CO)(PCy_3)M\text{—}C\begin{matrix}\nearrow OH\\ \searrow Me\end{matrix}\right]^+$$

and from protonation of metal-acyl anions neutral hydroxycarbene complexes of Cr and W were obtained [12]:



$$\left[(CO)_5M\text{—}C\begin{matrix}\nearrow\!\!O\\ \searrow R\end{matrix}\right]^- \xrightarrow{H^+} (CO)_5M\text{—}C\begin{matrix}\nearrow OH\\ \searrow R\end{matrix}$$

(R = Me, Ph; M = Cr, W)

A similar route has been used for the preparation of $Mn^{(I)}$ hydroxycarbene complexes [13]:

$$[MnX(COMe)(CO)_4]^- \xrightarrow{H^+} MnX[C(OH)Me](CO)_4$$

(X = Br, I)

These complexes behaved as relatively strong acids in water, giving eventually $MnMe(CO)_5$:

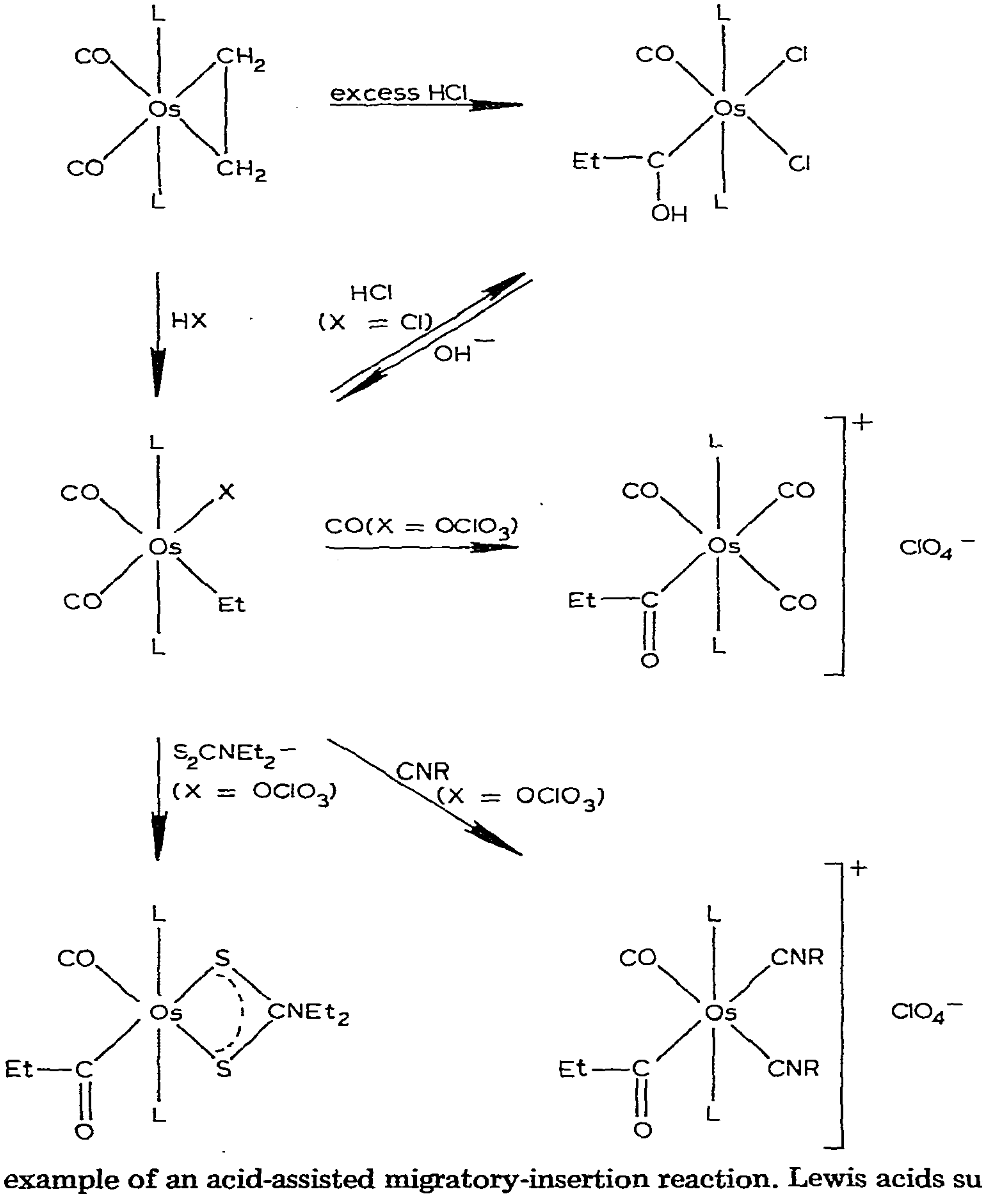
$$MnX[C(OH)Me](CO)_4 \xrightarrow{-H^+} [MnX(COMe)(CO)_4]^- \xrightarrow{-X^-} MnMe(CO)_4$$

The parallel between this system and $OsCl_2[C(OH)Et](CO)(PPh_3)_2$ is obvious. The conversion of $OsEtCl(CO)_2(PPh_3)_2$ to $OsCl_2[C(OH)Et(CO)(PPh_3)_2$ is a good

SCHEME 1

REACTIONS OF $Os(\eta^2\text{-}C_2H_4)(CO)_2(PPh_3)_2$

($L = PPh_3$; $X = Cl, I, O_2CCF_3, OClO_3$; $R = p$-tolyl)



example of an acid-assisted migratory-insertion reaction. Lewis acids such as $AlBr_3$ have this same ability to promote migration reactions [14].

The lability of the perchlorate group in $OsEt(OClO_3)(CO)_2(PPh_3)_2$ made this compound synthetically useful. Heating under carbon monoxide pressure yields $[Os(C(O)Et](CO)_3(PPh_3)_2]ClO_4$ (see Table 1 for IR data). A similar reaction using *p*-tolylisocyanide gives $[Os[C(O)Et](CO)(CNR)_2]ClO_4$. Heating $OsEt(OClO_3)(CO)_2(PPh_3)_2$ in benzene/ethanol with sodium diethyldithiocarbamate produces $Os[C(O)Et](S_2CNEt_2)(CO)(PPh_3)_2$.

Reactions of $Os(\eta^2\text{-}C_2H_4)(CO)_2(PPh_3)_2$ with other electrophiles were attempted less successfully. With halogens, $Os(\eta^2\text{-}C_2H_4)(CO)_2(PPh_3)_2$ yields $OsX_2(CO)_2(PPh_3)_2$. The fate of the ethylene moiety in these reactions was not investigated. Attempted reaction with methyl iodide resulted largely in the recovery of starting material contaminated with $OsI_2(CO)_2(PPh_3)_2$.

Experimental

General experimental conditions and instrumentation were as have been described previously [15].

$Os(\eta^2\text{-}C_2H_4)(CO)_2(PPh_3)_2$

$Os(CO)_2(PPh_3)_3$ [16] (1.00 g) was dissolved in benzene (50 ml) in a 250 ml flask which was flushed with ethylene, stoppered and placed in direct sunlight or under a tungsten-halogen lamp. A colourless solution resulted within 30 min of irradiation. Ethanol (75 ml) was added and the solution evaporated under reduced pressure to approx. 25 ml. Hexane (50 ml) was added and the white crystals filtered (0.6 g, 78%). A sample was recrystallised from dichloromethane ethanol. M.p. 165—169°C. Anal. Found: C, 59.82; H, 4.61; P, 7.87. $C_{40}H_{34}P_2O_2$ calcd.: C, 60.05; H, 4.28; P, 7.75%.

$Os(Et)I(CO)_2(PPh_3)_2$

$Os(\eta^2\text{-}C_2H_4)(CO)_2(PPh_3)_2$ (0.17 g) was dissolved in dichloromethane (10 ml). To this was added hydroiodic acid (0.1 ml) and ethanol (10 ml). The resultant pale green solution was evaporated under reduced pressure to yield white crystals which were recrystallised from dichloromethane/ethanol (0.19 g, 96%). M.p. 201—206°C. Anal. Found: C, 52.02; H, 4.10; P, 6.29. $C_{40}H_{35}P_2O_2IOs$ calcd.: C, 51.83; H, 3.81; P, 6.69%.

$Os(Et)(O_2CCF_3)(CO)_2(PPh_3)_2$

This complex was prepared in an analogous manner using trifluoroacetic acid (0.05 ml). Recrystallisation was from dichloromethane/ethanol, to give white needles (0.17 g, 88%). M.p. 193—196°C. Anal. Found: C, 55.22; H, 4.10; P, 6.35. $C_{42}H_{35}P_2O_4F_3Os$ calcd.: C, 55.25; H, 3.86; P. 6.79%.

$Os(Et)(OClO_3)(CO)_2(PPh_3)_2$

To $Os(\eta^2\text{-}C_2H_4)(CO)_2(PPh_3)_2$ (0.2 g) in dichloromethane (15 ml) was added perchloric acid (0.1 g, 70% aqueous) and ethanol (10 ml). The solution was evaporated to approx. 5 ml and seeded by scratching the walls of the vessel. The resultant white solid was recrystallised from dichloromethane/ethanol/cyclohexane to give lustrous white plates (0.18 g, 80%). M.p. 154—157°C. Anal. Found: C, 53.02; H, 4.67; P, 6.18. $C_{40}H_{35}P_2O_6ClOs$ calcd.: C, 53.41; H, 3.92; P, 6.89%.

$OsCl_2[C(OH)Et](CO)(PPh_3)_2$

To $Os(\eta^2\text{-}C_2H_4)(CO)_2(PPh_3)_2$ (0.3 g) dissolved in dichloromethane (20 ml) was added ethanol (15 ml) and hydrochloric acid (0.5 ml). Evaporation under reduced pressure produced a pale green solid which was recrystallised from dichloromethane/ethanol/hydrochloric acid to give white crystals (0.31 g, 94%). M.p. 225—230°C. Anal. Found: C, 55.44; H, 4.55. $C_{40}H_{36}P_2Cl_2O_2Os$ calcd.: C, 55.10; H, 4.16%.

$OsEtCl(CO)_2(PPh_3)_2$

(a) $OsCl_2[C(OH)Et](CO)(PPh_3)_2$ (0.2 g) was dissolved in dichloromethane (10 ml) and sodium methoxide (5 ml, 0.1 *M* in methanol) added. The solution was filtered to remove a fine precipitate of sodium chloride and ethanol (20 ml) added. Evaporation under reduced pressure gave white crystals which were recrystallised from dichloromethane/ethanol (0.17 g, 89%). M.p. 205—210°C. Anal. Found: C, 57.39; H, 4.53; P, 7.26. $C_{40}H_{35}P_2O_2ClOs$ calcd.: C, 57.50; H, 4.22; P, 7.42%.

(b) To $OsEt(OClO_3)(CO)_2(PPh_3)_2$ (0.1 g) dissolved in a minimum of dichloromethane was added lithium chloride (0.1 g) in ethanol (5 ml). On warming to remove dichloromethane, white crystals of the product were deposited, (0.08 g, 86%).

$[Os[C(O)Et](CO)_3(PPh_3)_2]ClO_4$

$Os(Et)(OClO_3)(CO)_2(PPh_3)_2$ (0.15 g) was dissolved in dichloromethane (20 ml) and subjected to carbon monoxide (20 psi) at 60°C for 2 h. On cooling, the solvent was evaporated to 5 ml and petroleum spirit added slowly to give a white crystalline precipitate. Recrystallisation from dichloromethane/ethanol gave a product as white photosensitive needles (0.13 g, 82%). M.p. 180—184°C. Anal. Found: C, 52.48; H, 4.01; P, 6.19. $C_{42}H_{35}P_2O_8ClOs$ calcd.: C, 52.79; H, 3.69; P, 6.48%.

$[Os[C(O)Et](CO)(CNC_7H_7)_2(PPh_3)_2]ClO_4$

$Os(Et)(OClO_3)(CO)_2(PPh_3)_2$ (0.1 g) and *p*-tolylisocyanide (0.05 g) were dissolved in dichloromethane (10 ml) and ethanol (10 ml). This solution was heated under reflux for 5 min and reduced to 5 ml. The addition of petroleum spirit gave a pale yellow precipitate which gave cream crystals of the product on recrystallisation from dichloromethane/cyclohexane/ethanol (0.1 g, 80%). M.p. 203—205°C. Anal. Found: C, 59.17; H, 4.64; N, 2.60. $C_{56}H_{49}N_2O_6P_2ClOs$ calcd.: C, 59.31; H, 4.37; N, 2.47%.

$Os[C(O)Et](\eta^2\text{-}S_2CNEt_2)(CO)(PPh_3)_2$

To $Os(Et)(OClO_3)(CO)_2(PPh_3)_2$ (0.15 g) dissolved in benzene (10 ml) was added sodium diethyldithiocarbamate (0.07 g) dissolved in ethanol (10 ml). The solution was heated under reflux for 10 min, reduced in volume to ca. 5 ml and a solid obtained by the addition of hexane. Recrystallization from dichloromethane/ethanol gave the product as cream crystals (0.14 g, 89%). M.p. 112—114°C. Anal. Found: C, 56.88; H, 5.02; N, 1.38; P, 6.30. $C_{45}H_{45}NO_2P_2S_2Os$ calcd.: C, 57.01; H, 4.79; N, 1.48; P, 6.54%.

Acknowledgements

We thank the New Zealand Universities Grants Committee for grants towards instrumental facilities and the award of a Postgraduate Scholarship to K.R. Grundy.

References

1 W.R. Roper and L.J. Wright, J. Organometal. Chem., 142 (1977) C1.
2 C.E.L. Headford and W.R. Roper, J. Organometal. Chem., 198 (1980) C7.
3 W.R. Roper, G.E. Taylor, J.M. Waters and L.J. Wright, J. Organometal. Chem., 182 (1979) C46.
4 H. Berke and R. Hoffman, J. Amer. Chem. Soc., 100 (1978) 7224.
5 F. L'Eplattenier and C. Pelichet, Helv. Chim. Acta, 53 (1970) 1091.
6 B.E. Cavit,, K.R. Grundy and W.R. Roper, J. Chem. Soc. Chem. Commun., (1972) 60.
7 B.F.G. Johnson and J.A. Segal, J. Chem. Soc. Chem. Commun., (1972) 1312.
8 R.D.W. Kemmitt and D.I. Nichols, J. Chem. Soc. (A)., (1969) 1577.
9 R.D.W. Kemmitt, B.Y. Kimura, G.W. Littlecott and R.D. Moore, J. Organometal. Chem., 44 (1972) 403.
10 R. Cramer, J. Amer. Chem. Soc., 87 (1965) 4717.
11 M.L.H. Green, L.C. Mitchard and M.G. Swanwick, J. Chem. Soc. (A)., (1971) 794.
12 E.O. Fischer, G. Kreis and F.R. Kreissl, J. Organometal. Chem., 56 (1973) C37.
13 J.R. Moss, M. Green and F.G.A. Stone, J. Chem. Soc. Dalton, (1973) 975.
14 S.B. Butts, E.M. Holt, S.H. Strauss, N.W. Alcock, R.E. Stimson and D.F. Shriver, J. Amer. Chem. Soc., 101 (1979) 5864.
15 T.J. Collins and W.R. Roper, J. Organometal. Chem., 159 (1978) 73.
16 D.H. Farrar, K.R. Grundy, N.C. Payne, W.R. Roper and A. Walker, J. Amer. Chem. Soc., 101 (1979) 6577.