Transition-metal Nitrosyl Compounds. Part X.[1] A Study of Olefin Rotation in $[Os(CO)NO(C_2H_4)(PPh_3)_2][PF_6]$

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The reaction of $[Os(CO)NO(PPh_3)_2Cl]$ first with silver hexafluorophosphate and then ethylene leads to formation of the PF_6^- salt of the cation $[Os(CO)NO(C_2H_4)(PPh_3)_2]^+$. This cation is thought to possess a trigonal bipyramidal geometry in which the CO, NO, and C_2H_4 ligands occupy equatorial positions. Under ambient conditions the ethylene rotates and variable temperature ^{13}C n.m.r. data provide direct experimental evidence that this type of rotation occurs *via* the metal–olefin bond. The value of $\Delta G^{\ddagger}_{T_c}$ was determined as 9·5 ± 0·2 kcal mol^{-1}.

In recent years much effort has been directed to studies of the rotation of olefins, particularly ethylene, in transition-metal systems. Elegant work by Cramer[2] on square-planar rhodium(I)–olefin complexes first led to the suggestion that the rotation of ethylene could occur about the metal–olefin axis [mechanism (a), Figure 1]. On the basis of his experimental evidence, however, Cramer could not rule out the alternative rotational mode about the olefinic C=C axis [mechanism (b), Figure 1].

Since Cramer's original report others have followed which are concerned particularly with the factors, both electronic and steric, that affect the magnitude of the rotational barrier in a series of rhodium(I),[2-6] iridium(I),[6-8] and platinum(II)[9-12] olefin complexes. In all

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[1] Part IX, B. F. G. Johnson and J. A. Segal, *J.C.S. Dalton*, 1974, 981.

[2] R. Cramer, *J. Amer. Chem. Soc.*, 1964, **86**, 217.

[3] R. Cramer, J. B. Kline, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1969, **91**, 2519.

[4] R. Cramer and J. J. Mrowca, *Inorg. Chim. Acta*, 1971, 528.

[5] R. Cramer and G. S. Reddy, *Inorg. Chem.*, 1973, **12**, 346.

[6] K. Moseley, J. W. Kang, and P. M. Maitlis, *J. Chem. Soc.* (*A*), 1970, 2875.

[7] A. L. Onderdelinden and A. van der Ent, *Inorg. Chim. Acta*, 1972, **6**, 420.

[8] K. van Putte and A. van der Ent, *Inorg. Chim. Acta*, 1973, **7**, 497.

[9] C. E. Holloway, G. Hulley, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc.* (*A*), 1969, 53.

[10] C. E. Holloway, G. Hulley, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc.* (*A*), 1970, 1653.

[11] J. Ashley-Smith, I. Douek, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1972, 1776.

[12] J. Ashley-Smith, I. Douek, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1974, 128.

the assumption has been made that rotation occurs *via* mechanism (a) (Figure 1). Initially this assumption appeared justified since rotation about the C=C axis was thought to lead to simultaneous rupture of the metal–olefin σ- and π-bonds, hence causing ligand dissociation. However it is now thought that this need not occur. Alternative bonding modes which were neglected in the initial studies must be considered. For example, Jonassen and co-workers[13] have put forward a new bonding arrangement for olefin and acetylene complexes of platinum (see Figure 2). In such a scheme rotation about the C–C bond need not necessarily lead to olefin dissociation. Furthermore for the situation in which the olefin occupies a position in the *xy* plane of the molecule (Figure 3) it may be argued that δ-overlap of the olefin π* orbital with the d_{yz} metal orbital is conceivable.[13]

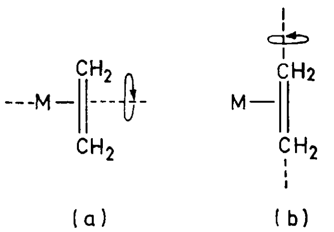

FIGURE 1

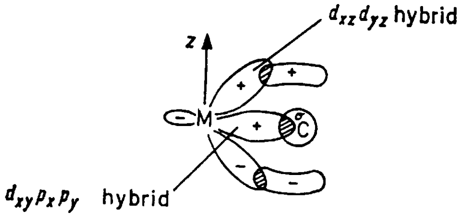

FIGURE 2

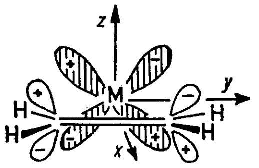

FIGURE 3 Olefin π* orbital orientated for δ overlap

Tentative evidence supporting the rotational mode (a) (Figure 1) has been provided by Paiaro[14] from studies of the epimerisation rates of diastereoisomeric platinum(II)–olefin complexes and by Lewis and his co-workers[9] from the effects of steric crowding on the rotational barriers of olefins in species of the type [PtCl(olefin)(acac)]. However *direct* experimental evidence has been lacking. The work described in this paper was carried out specifically to provide such evidence.[15]

All ethylene complexes for which detailed rotational data are currently available possess a plane of symmetry bisecting the olefinic carbon–carbon bond in their ground state geometries (see *e.g.* Figure 4 †). Rotation may be observed in these species provided that the arrangement of the other ligands about the metal imposes a different chemical environment on the protons bound to each *side* of the olefinic carbon atoms. Thus in the example shown in Figure 4 the protons H_0 are adjacent to an O-atom whereas the protons H_x are adjacent to the halogen atom X. For this ground-state geometry (*i.e.* at the low-temperature limit) a ^1H n.m.r. spectrum of the AA′BB′ type is expected which at higher temperatures will collapse to single A_4 line. However, although rotation may be detected on this basis the experimental evidence obtainable from such systems will *not* differentiate between the two possible rotational modes (*i.e.* 1a or 1b). The *mode of rotation* can only be determined from n.m.r. spectral data provided that the two *ends* of the olefin are in different chemical environments. Thus if a plane of symmetry does exist in the ground state geometry of the molecule then the olefinic C–C axis must lie in it (as in Figure 5). The ^1H n.m.r. spectrum for ethylene co-ordinated in this configuration will again be of the AA′BB′ type. However, at the high-temperature limit rotation about the co-ordination axis is expected to lead to an A_4 spectrum whereas rotation about the olefin axis should leave the AA′BB′ pattern unchanged. For the ^{13}C n.m.r. spectrum even more obvious differences may be predicted. At lower temperatures two signals corresponding to C_x and C_y should be observed and, if rotation occurs about the co-ordination axis, these signals should collapse to a single resonance (*i.e.* $C_x \rightleftharpoons C_y$) whereas if rotation occurs about the olefin axis then two signals should still be observed since C_x and C_y will remain

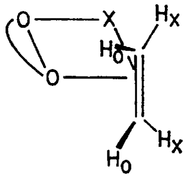

FIGURE 4

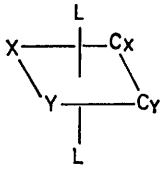

FIGURE 5

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† *Note added in proof:* H. Alt, N. Herberhold, C. G. Kreiter, and H. Straek, *J. Organometallic Chem.*, 1974, **77**, 353, have reported n.m.r. studies on the complex [(η-cp)Cr(CO)NO(C_2H_4)] which has no symmetry planes and shows an ABCD spectrum for ethylene protons in the ground-state configuration. We also note that these authors have obtained the very low rotational-energy barrier $\Delta G^{\ddagger}_{T_c} = 8{\cdot}4$ kcal mol^{-1} for the complex [(η-cp)Mn$(CO)_2(C_2H_4)$]. This is the lowest barrier obtained for olefin rotation in a species for which the ground-state spectrum has been attained, see further in text.

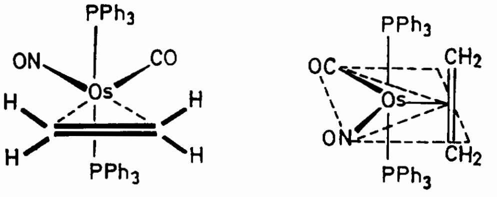
[13] J. H. Nelson, K. S. Wheelock, L. C. Cusachs, and H. B. Jonassen, *J. Amer. Chem. Soc.*, 1969, **91**, 7005.

[14] G. Paiaro, *Organometallic Chem. Rev.* (*A*), 1970, **6**, 319.

[15] For a preliminary account see B. F. G. Johnson and J. A. Segal, *J.C.S. Chem. Comm.*, 1972, 1312.

chemically distinct. Thus a clear differentiation between the two possible rotational modes may be made.

We have prepared the complex $[Os(CO)NO(C_2H_4)(PPh_3)_2][PF_6]$ which apparently satisfies the above criterion. The ground-state configuration about the osmium atom was established as follows. Comparison with the known structure of the cation $[Os(CO)_2NO(PPh_3)_2]^+$ [16] and other similar species[17] leads to the assumption that the cation possesses an essentially trigonal bipyramidal geometry with axial phosphine ligands (Figure 6a, b). The fact that *equivalent* ^{31}P coupling to each of the ethylene protons is observed in the high-temperature limiting ^1H n.m.r. spectrum (Figure 7) tends to support this view as it indicates that both phosphorus atoms are in equivalent environments.



(a) (b)

FIGURE 6

In the low temperature (−80 °C) ^{13}C n.m.r. spectrum, run in $(CD_3)_2CO$ (Figure 8), two resonances of equal intensity are observed at 54·4 and 43·6 p.p.m.* A similar spectrum is observed in CD_2Cl_2 except that the former signal is masked by solvent absorptions. These results are taken to indicate that the ethylene molecule does occupy an *in plane* orientation in a *pseudo* octahedral ground-state geometry such that the two ethylenic carbon atoms are in different chemical environments *viz* one *trans* to NO, the other *trans* to CO (Figure 6a). The room-temperature (20 °C) ^{13}C n.m.r. spectrum in CD_2Cl_2 or $(CD_3)_2CO$ shows a single resonance for the ethylenic carbon nuclei at 49·3 p.p.m. in which ^{31}P coupling has *not* been resolved.

At −90 °C the ^1H n.m.r. spectrum of the complex in CD_2Cl_2 +10% CF_2Cl_2 shows two signals of equal intensity (2H) centred at τ 6·51 and 8·77 (measured relative to the CH_2Cl_2 resonance at τ 4·65). The fully resolved low-temperature limiting spectrum has not been obtained. On warming, coalescence occurs at −65 °C and at the high-temperature limit a single 1 : 2 : 1 triplet, corresponding to *four* protons is observed at τ 7·38 with J_{PH} = 5·3 Hz. Since ^{31}P–H coupling is maintained in the high-temperature limit and does not vary over a sizeable temperature range (above coalescence) any contribution of an intermolecular exchange mechanism may be regarded as insignificant (the variation of the spectrum as a function of temperature is shown in Figure 7). Assuming the ground-state configuration shown (Figure 6a) it is clear that coalescence can only occur in both the ^1H and ^{13}C n.m.r. spectra provided that rotation occurs about the metal–olefin bond.

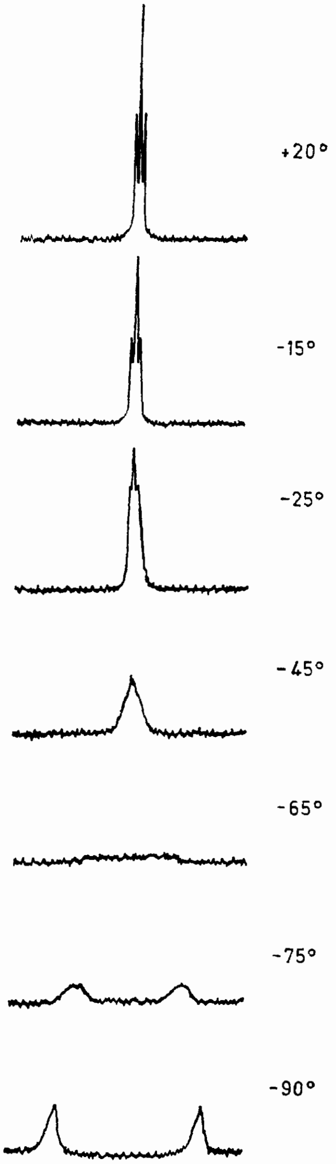


FIGURE 7 ^1H N.m.r. spectra (τ 6—9) of $[Os(CO)NO(C_2H_4)(PPh_3)_2][PF_6]$ in the temperature range +20 to −90 °C

Other geometries for the complex are of course possible but whatever five-co-ordinate geometry is assumed the

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* These may be assigned to olefinic carbon atoms.[18] In addition a triplet is seen at 182·9 p.p.m. with J_{PC} 8 Hz (Figure 8) and is attributed to the carbon of the CO group which is coupled to two equivalent ^{31}P nuclei. This signal was only well-resolved at low temperature (−80 °C) a fact which may be explained in terms of the increased viscosity of the solvent reducing the spin–lattice relaxation time.[19]

[16] G. R. Clark, K. R. Grundy, W. R. Roper, J. M. Waters, and K. R. Whittle, *J.C.S. Chem. Comm.*, 1972, 119.

[17] See *e.g.* A. R. Luxmoore and M. Truter, *Acta Cryst.*, 1962, **15**, 1117; C. Pedone and A. Sirign, *Inorg. Chem.*, 1968, **7**, 2614; J. K. Stalick and J. A. Ibers, *Inorg. Chem.*, 1969, **8**, 419.

[18] M. H. Chisholm, H. C. Clark, L. E. Manzer, and J. B. Stothers, *J. Amer. Chem. Soc.*, 1972, **94**, 5087.

[19] See *e.g.* T. C. Farrar and E. D. Becker, 'Pulse and Fourier Transform NMR,' Academic Press, 1971, p. 49.

experimental results define the mode of rotation. However, the possibility of *simultaneous* rotation about the olefin and co-ordination axes cannot be excluded. This simultaneous motion about the two axes has been considered previously in early broad-line n.m.r. studies[20] on Ziese's salt.

The recent work of Osborn[21] and Takats[22] and their co-authors on [Fe(CO)$_4$(olen)] (olen = olefin with bulky electron-withdrawing groups) has drawn our attention to the idea that olefin rotation in five-co-ordinate complexes may be accompanied by the ligand rearrangement normally interpreted as Berry[23] pseudo-rotation. Coupling of the two effects apparently occurs when the olefinic substituents interact with the other ligands and thus obstruct their motion[24] (in certain circumstances this might severely restrict the amplitude of the dihedral angular oscillations in the Berry process). The result is that the energy barriers obtained are much higher than normally found in [Fe(CO)$_4$L] species, as, for example, [Fe(CO)$_4$(pyridine)].[25] In the complex [Os(CO)NO(C$_2$H$_4$)(PPh$_3$)$_2$][PF$_6$] Berry pseudo-rotation may contribute to the overall rearrangement process but alone it cannot be responsible for the observed effects. The low rotational barrier (for a system with bulky phosphine groups), see below, suggests that the degree of coupling would not be in any way as great as in the aforementioned systems. However whether pseudo-rotation occurs or not is immaterial to the interpretation of the rotational mode.* We also note that interactions with other ligands invariably occur when co-ordinated olefins rotate, this being partly responsible for the existence of a barrier as is seen, for example, in the *cis*-PtX(olefin)L$_2$] systems studied by Lewis.[9-12] Whether the other ligands themselves are rigid or in motion should not alter the basic phenomenon unless interactions are so great as to restrict the motion of the olefin either totally or to cause oscillation rather than rotation: normally the effect of ligands in motion may only be to produce a *varying* barrier.

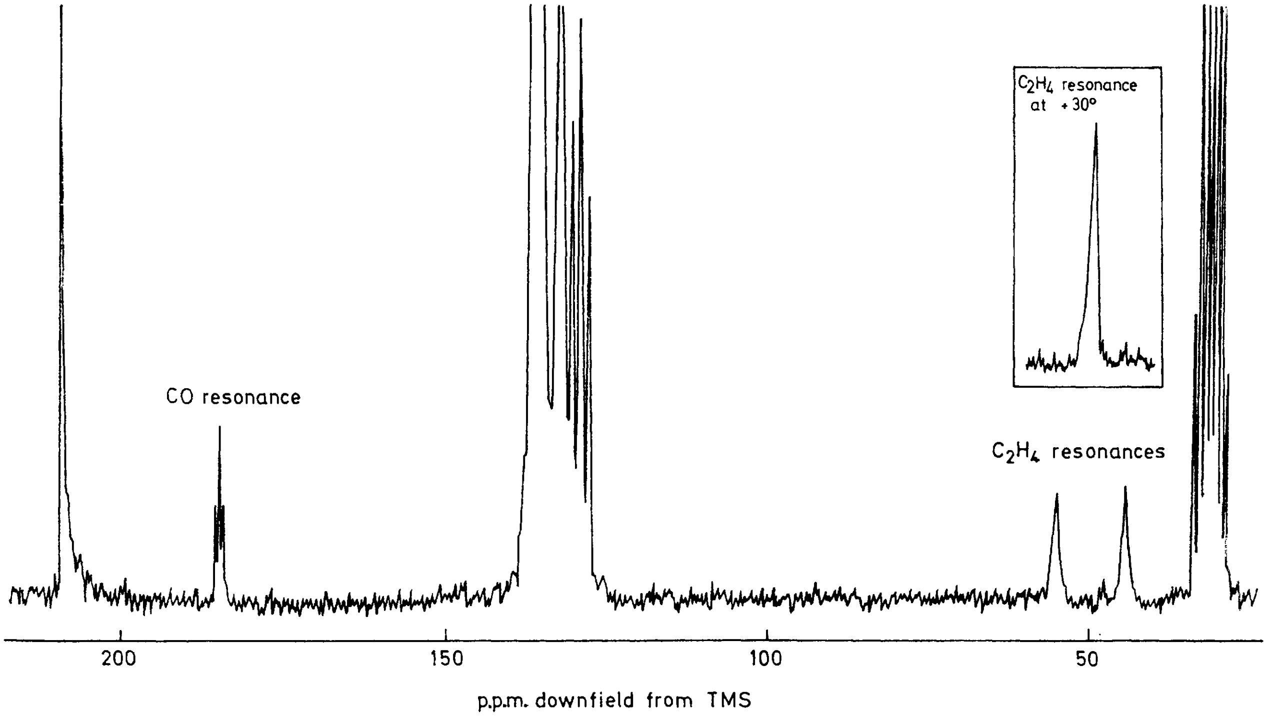

FIGURE 8 ^{13}C N.m.r. spectrum of [Os(CO)NO(C$_2$H$_4$)(PPh$_3$)$_2$][PF$_6$] at −80 °C in [^{2}H$_6$]acetone

As the ethylene molecule rotates each proton passes between two extreme chemical environments (*via* a transition state as represented in Figure 6b). Rate data can be obtained for the exchange between these two equally populated sites by the use of approximate formulae provided that the natural line widths of resonances for each site are negligible compared to their separation on a frequency scale.[9] Use of such formulae gives an expression (see Experimental section) from which a $\Delta G^{\ddagger}_{T_c}$ value of 9·5 ± 0·2 kcal mol^{-1} was obtained.

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* That a turnstile mechanism might operate is also to be considered. This would effectively have to interchange the CO and NO groups to be equivalent to the rotation process and seems energetically unfavourable compared with the olefinic CH$_2$ interchange in the pseudo-octahedral geometry.

[20] S. Maričić, C. R. Redpath, and J. A. S. Smith, *J. Chem. Soc.*, 1963, 4905.

[21] S. T. Wilson, N. J. Coville, J. R. Shapely, and J. A. Osborn, *J. Amer. Chem. Soc.*, 1974, **96**, 4038.

[22] L. Kruczynski, L. K. K. LiShingMan, and J. Takats, *J. Amer. Chem. Soc.*, 1974, **96**, 4006.

[23] R. S. Berry, *J. Chem. Phys.*, 1960, **32**, 933.

[24] E. L. Muetterties, P. Meakin, and R. Hoffmann, *J. Amer. Chem. Soc.*, 1972, **94**, 5674.

[25] F. A. Cotton and J. M. Troup, *J. Amer. Chem. Soc.*, 1974, **96**, 3438.

This value is smaller than those recorded by Cramer[3-5] for the cyclopentadienylrhodium systems (which range from *ca.* 11·7 to 17·0 kcal mol^{-1}) and by Lewis and his co-workers[9-12] for various platinum(II) systems (which range from 10·2 to 16·0 kcal mol^{-1}) but is apparently larger than that found for the species $[Rh(\pi\text{-}Cp)(C_2H_4)_2]\cdot HgCl_2$,[4] $[Ir(C_2F_4)(C_2H_4)(acac)]$,[8] and $[Ir(C_2H_4)_4Cl]$[7,8] (in toluene but not in chloroform), all of which cannot be frozen out on the n.m.r. time scale and are thought to have $\Delta G^{\ddagger}_{T_c}$ values considerably lower than 10 kcal mol^{-1}. van Putte and van der Ent[8] have obtained the very low activation-energy values of 1·6 and 5·3 kcal mol^{-1} for the rotational processes of the axial and equatorial ethylene ligands of $[Ir(C_2H_4)_4Cl]$ from proton spin-relaxation studies. However, these values relate to the solid-state behaviour of the complex and therefore they cannot be directly compared with the results of solution n.m.r. studies.

Others[9-12] have examined the factors responsible for the variation of the rotational barriers in a series of Pt^{II} complexes. Broadly speaking the *difference* between the steric interactions in the ground and excited states is thought to be the major factor contributing to the variation found although it is difficult if not impossible to completely differentiate between the electronic and steric effects. This problem has been explained in detail elsewhere.[12]

EXPERIMENTAL

The preparation of the complex and all manipulations involving it were carried out under dry oxygen-free nitrogen. N.m.r. tubes were filled with deuteriated solvents by vacuum distillation and then sealed. ^{1}H N.m.r. spectra were measured in 5-mm tubes on a Varian Associates HA-100 or XL-100 spectrometer at 100 MHz and ^{13}C n.m.r. spectra were measured in 12-mm tubes on a Varian Associates XL-100 spectrometer at 25·14 MHz. The proton spectra were calibrated either directly against Me_4Si or against the CH_2Cl_2 resonance in CD_2Cl_2 taking its position as 24·65; the ^{13}C spectra were measured relative to a solvent deuterium lock and converted into p.p.m. downfield from the Me_4Si signal in the same solvent. Probe temperatures were measured using the precalibrated internal chemical shift of a methanol sample. The value of the free energy of activation was calculated using the expression,

$$\Delta G^{\ddagger}_{T_c} = -RT_c \ln \frac{\pi \Delta\nu h}{\sqrt{2}kT_c}$$

where $\Delta\nu$ represents the chemical shift of the coalescing peaks in the absence of exchange, T_c represents the coalescence temperature, and R, k, and h have their normal thermodynamic significance. The value obtained is approximate[11,12] and is subject to the limitations outlined by Raban and his co-workers[26] (we note especially that $\Delta G^{\ddagger}_{T_c}$ in the above equation is insensitive to variations in $\Delta\nu$ when $\Delta\nu$ is large).

Carbonyl(ethylene)nitrosylbis(triphenylphosphine)osmium-(0) Hexafluorophosphate.—A suspension of $[OsHCl(CO)(PPh_3)_3]$ (0·300 g) and *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide (0·105 g) in ethanol (15 ml) was stirred under reflux for 3 h. The resultant brown suspension was filtered off and taken up in dichloromethane (25 ml) to give a red solution. Silver hexafluorophosphate (0·069 g) in acetone (1 ml) was added to the solution causing an immediate colour change to yellow. The mixture was shaken for a few seconds and then rapidly filtered through Kieselguhr, the filtrate being collected in a flask cooled to −196 °C. The frozen solution was then allowed to warm up to room temperature under an atmosphere of ethylene and as soon as possible it was saturated with this gas causing a colour change to pale yellow. Pentane was carefully added to the solution causing precipitation of the microcrystalline product (0·250 g) which was filtered off, washed with pentane, and dried *in vacuo*. The product may be recrystallised from dichloromethane–pentane; if ether is used instead of pentane, a crystalline product is obtained but this contains residual ether, as observed by ^{1}H n.m.r., which could not be removed even on prolonged pumping (Found: C, 49·4; H, 3·8; N, 1·6; P, 9·9. $C_{39}H_{34}F_6NO_2P_3Os$ requires C, 49·5; H, 3·6; N, 1·5; P, 9·8%). I.r. spectrum (CH_2Cl_2): ν(CO) 2029vs and ν(NO) 1747vs. The complex is best stored under ethylene gas as it tends to lose ethylene both *in vacuo* and under a nitrogen atmosphere.

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[4/943 *Received*, 14*th May*, 1974]

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[26] D. Kost, E. H. Carlson, and M. Raban, *Chem. Comm.*, 1971, 656.