Carbene Complexes. Part 15.[1] The Synthesis and Properties of Electron-rich Olefin-derived Mono- and Oligo-carbenenitrosyl-ruthenium, -osmium, and -nickel Complexes †

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An electron-rich olefin $[{:}\overline{CN(R)CH_2CH_2N}R]_2$ ($L^R{}_2$; R = Me, Et, or CH_2Ph) readily reduces $[RuCl_3(NO)(PPh_3)_2]$ to $[RuCl(NO)(PPh_3)_2]$ which then (*a*) (R = Me) reacts with an excess of olefin to give the dioxygen- and water-sensitive $[Ru(L^{Me})_4(NO)]Cl$ (1), or (*b*) (R = CH_2Ph) yields $[RuCl(L^{CH_2Ph})_2(NO)]$ (3). Complex (1) is readily oxidised by Ag^+ to give *trans*-$[RuCl(L^{Me})_4(NO)]X_2$ (X = $[BF_4]$ or $[ClO_4]$) and reacts with CO to afford *trans*-$[Ru(CO)Cl(L^{Me})_4]Cl$. In contrast, complex (3) is oxidised by MeI or $PhCH_2Cl$ to give $[RuMe(Cl)I(L^{CH_2Ph})_2(NO)]$ (8) or $[RuCl_3(L^{CH_2Ph})_2(NO)]$ (9), respectively, and with CO gives $[Ru(CO)Cl(L^{CH_2Ph})_2(NO)]$. Complex (3) also undergoes oxidative addition with a heavy dihalogen to give $[Ru(Cl)I_2(L^{CH_2Ph})_2(NO)]$ or $[RuBr_2Cl(L^{CH_2Ph})_2(NO)]$ which differ in configuration from (8) or (9). The complex $[OsCl_3(NO)(PPh_3)_2]$ is only sluggishly reduced by $L^{Me}{}_2$, finally affording the exceptionally air- water-, or dissolution-sensitive $[Os(L^{Me})_4(NO)]Cl$ (2), and $L^{CH_2Ph}{}_2$ does not effect reduction but yields $[OsCl_2(L^{CH_2Ph})_3(NO)]Cl$ and *trans*-$[OsCl(L^{CH_2Ph})_4(NO)]Cl_2$. Complex (2) is easily oxidised: with $Ag[BF_4]$ or CH_2Cl_2 it forms *trans*-$[OsCl(L^{Me})_4(NO)][BF_4]_2$ or *trans*-$[OsCl(L^{Me})_4(NO)]Cl_2$ respectively. Whereas only one PPh_3 is lost from $[Ru(NO)_2(PPh_3)_2]$ and $L^{Et}{}_2$ yielding $[RuL^{Et}(NO)_2PPh_3]$, both are displaced from $[Ni(NO)(PPh_3)_2X]$ to give $[Ni(L^R)_2(NO)X]$ (X = Cl, R = Et; X = Br, R = CH_2Ph). Spectroscopic data (^1H and ^{13}C n.m.r. and i.r.) of the new complexes are reported. Many of the complexes exhibit complicated ^1H n.m.r. spectra because of the inequivalence of $N-CH_2Ph$ protons or $N-CH_3$ groups, caused by restricted rotation [$\Delta G^\ddagger$ (rotation) >25 kcal mol^{-1} about $M-C_{carb.}$ bonds]. Several trends are noted: as the metal charge increases (neutral < unipositive < dipositive) (*i*) $\nu(CN_2)$ increases, (*ii*) $\delta(^{13}C_{carb.})$ becomes more shielded, (*iii*) the barrier to $Ru-C_{carb.}$ rotation increases, and (*iv*) complex stability increases, which are compatible with the progressively increased amidinium nature of the carbene ligand.

ALTHOUGH nitrosyls of ruthenium or osmium are well known (*e.g.* refs. 2—8), carbenenitrosyl-ruthenium or -osmium complexes had not been reported (and indeed only a few carbeneosmium complexes are known [1,9,10]). We now provide details on a number of such complexes, (1)—(16) (see Scheme and Table 1). We have previously shown that PPh_3 is readily displaced from the coordination sphere of ruthenium (or another platinum-group metal) by the ligand ${:}\overline{CN(R)CH_2CH_2N}R$ (L^R; R = Me, Et, or CH_2Ph) on reaction with the olefin $L^R{}_2$.[1,11,12] We now report on the reaction of the latter (mainly $L^{Me}{}_2$ or $L^{CH_2Ph}{}_2$) with the stable and readily accessible $[RuCl_3(NO)(PPh_3)_2]$ (17),[5] $[OsCl_3(NO)(PPh_3)_2]$ (18),[2] $[Ni(NO)(PPh_3)_2X]$ (19; X = Br or Cl),[13] or $[Ru(NO)_2(PPh_3)_2]$ (20).[14]

RESULTS AND DISCUSSION

There is an interesting contrast, not observed before,[1,15,16] between the olefins $L^{Me}{}_2$ and $L^{CH_2Ph}{}_2$ in terms of their reactivity towards $[MCl_3(NO)(PPh_3)_2]$ [M = Ru (17) or Os (18)]. The *initial* mode of reaction with $L^R{}_2$ and complex (17) was reduction [equation (1)]. This occurred almost instantly at 25 °C in toluene (or thf) and is clearly superior to the zinc–tetrahydrofuran (thf) method.[17] The reduction is most conveniently carried out by using a non-carbene complex-forming electron-rich olefin,[18] such as tetrakis(dimethylamino)ethylene or tetrapyrrolidinylethylene, when no further reaction occurs, even with an excess of olefin in boiling toluene. Heating $[RuCl(NO)(PPh_3)_2]$, (21), with an excess of $L^{Me}{}_2$ in toluene caused precipitation of a thermally stable, but exceptionally air-, water-, and solution-sensitive, crimson complex with analytical and chemical properties indicative of $[Ru(L^{Me})_4(NO)]Cl$, (1), *ca.* 95% pure, directly from the reaction mixture {and isoelectronic with the known cations $[Ru(NO)(dppe)_2]^+$ (dppe = $Ph_2P[CH_2]_2PPh_2$),[8,19] $[Ru(CO)_2(PPh_3)_2]^+$,[8] and $[Ru(CO)(NO)(PPh_3)_3]^+$ (ref. 8)}. Further purification was not possible because of its rapid decomposition

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† No reprints available.

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in solution (*e.g.* in CH_2Cl_2 decomposition was complete within 1 h and attempts to recrystallise by low-temperature mixed-solvent methods only afforded partially decomposed oils). Reduction of the complex $[OsCl_3(NO)(PPh_3)_2]$ (18) is more difficult: L^{Me}_2 slowly reduced (18) in refluxing xylene, presumably to give $[OsCl(NO)(PPh_3)_2]$. However, unlike the ruthenium analogue, this complex has not been isolated because the olefin appears to react more quickly with it than its rate of formation. The only isolated product was the deep purple-mauve $[Os(L^{Me})_4(NO)]Cl$ (2), which is even more sensitive to oxidation than (1); complete decomposition in CH_2Cl_2 occurred within 5 min, even below −50 °C.

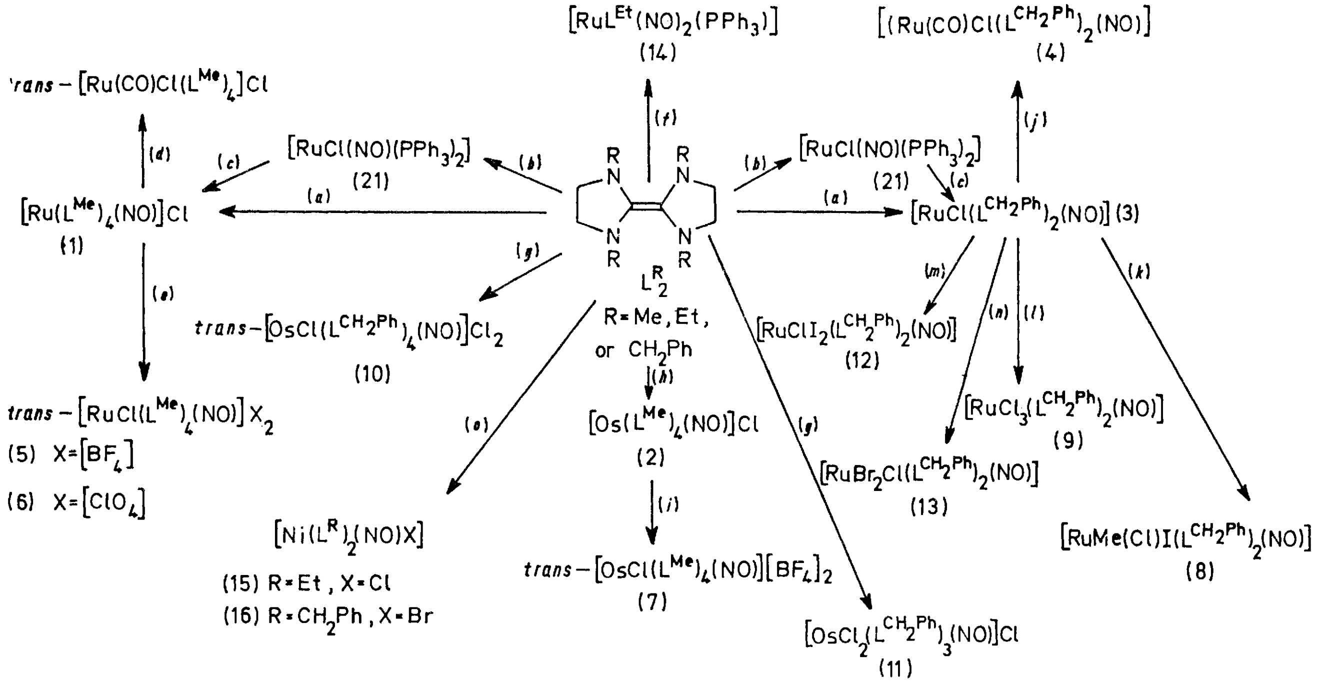
TABLE 1

Carbenenitrosyl-ruthenium, -osmium, and -nickel complexes and their characterisation [a]

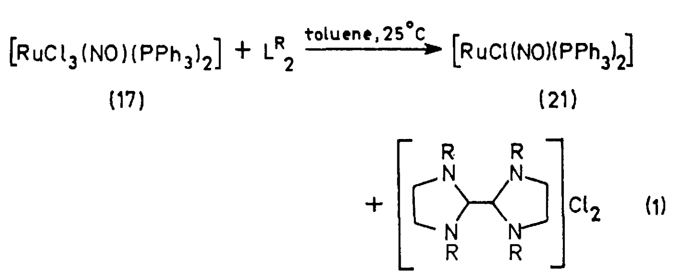
Complex	Yield (%)	M.p. (θ_c/°C)	Colour	Analysis (%) [b] C	H	N
(1) $[Ru(L^{Me})_4(NO)]Cl$ [c]	80	209 (decomp.)	Crimson	40.4 (42.9)	6.7 (7.4)	21.2 (22.5)
(2) $[Os(L^{Me})_4(NO)]Cl$ [d]	65	>200 (slow decomp.)	Purple	37.1 (36.8)	6.2(6.2)	19.2 (19.3)
(3) $[RuCl(L^{CH_2Ph})_2(NO)]$	95	223 (decomp.)	Ultramarine	61.1 (61.2)	5.1 (5.4)	10.4 (10.5)
(4) $[Ru(CO)Cl(L^{CH_2Ph})_2(NO)]$	90	190	Orange	60.3 (60.5)	5.3 (5.2)	10.1 (10.1)
(5) *trans*-$[RuCl(L^{Me})_4(NO)][BF_4]_2$	95	235 (decomp.)	Yellow	33.0 (32.8)	5.8 (5.5)	17.0 (17.2)
(6) *trans*-$[RuCl(L^{Me})_4(NO)][ClO_4]_2$	95	188	Yellow	31.5 (31.7)	5.3 (5.3)	16.5 (16.6)
(7) *trans*-$[OsCl(L^{Me})_4(NO)][BF_4]_2$	90	310	Yellow	29.6 (29.2)	5.0 (4.9)	15.2 (15.3)
(8) $[RuMe(Cl)I(L^{CH_2Ph})_2(NO)]$	75	156 (decomp.)	Orange-brown	51.9 (51.9)	4.9 (4.9)	8.5 (8.6)
(9) $[RuCl_3(L^{CH_2Ph})_2(NO)]$	70		Pale green	55.1 (55.3)	5.2 (4.9)	9.8 (9.5)
(10) *trans*-$[OsCl(L^{CH_2Ph})_4(NO)]Cl_2$	60	223	Lemon-yellow	61.1 (61.5)	5.6 (5.5)	9.7 (9.5)
(11) $[OsCl_2(L^{CH_2Ph})_3(NO)]Cl$	35	204 (decomp.)	Orange-yellow	51.3 (51.0)	5.0 (4.7)	7.9 (7.8) [e]
(12) $[RuClI_2(L^{CH_2Ph})_2(NO)]$	90	214	Red-brown	44.3 (44.3)	4.0 (3.9)	7.4 (7.6)
(13) $[RuBr_2Cl(L^{CH_2Ph})_2(NO)]$	80	226	Orange-brown	49.3 (49.4)	4.6 (4.4)	8.6 (8.5)
(14) $[RuL^{Et}(NO)_2(PPh_3)]$	30	117 (decomp.)	Purple-brown	55.0 (54.6)	5.4 (5.3)	10.3 (10.2)
(15) $[NiCl(L^{Et})_2(NO)]$	80	84 (decomp.)	Very dark blue	45.0 (44.7)	7.3 (7.5)	18.3 (18.6)
(16) $[NiBr(L^{CH_2Ph})_2(NO)]$	95	162	Very dark blue	61.2 (61.0)	5.5 (5.4)	10.5 (10.5)

[a] $L^R = \overline{{:}CN(R)CH_2CH_2N}R$ (R = Me, Et, or CH_2Ph). [b] Calculated values are given in parentheses. [c] Analysis figures quoted were obtained from the product direct from the reaction and correspond exactly to an empirical formula of $C_{20}H_{40}ClN_9ORu$ {*i.e.* $[Ru(L^{Me})_4(NO)]Cl$}, and a purity of *ca.* 95%. The extremely oxygen-sensitive nature of the complex and its rapid (*ca.* 20 min) decomposition in solvents (see text) has prevented recrystallisation. Cl, 6.0 (6.3%). [d] Cl, 5.6 (5.5%). [e] Calculated for $2CH_2Cl_2$ adduct.

Complexes (1) and (2) were readily oxidised by silver salts such as $Ag[BF_4]$ to give very stable dicationic



SCHEME Synthetic routes to and reactions of carbenenitrosyl-ruthenium, -osmium, and -nickel complexes. (*a*) $[RuCl(NO)(PPh_3)_2]$, toluene, 110 °C; (*b*) $[RuCl_3(NO)(PPh_3)_2]$, toluene, 25 °C; (*c*) excess of L^R_2, toluene, 110 °C; (*d*) CO, CH_2Cl_2, 25 °C; (*e*) AgX (X = $[BF_4]$ or $[ClO_4]$), CH_2Cl_2, 25 °C; (*f*) $[Ru(NO)_2(PPh_3)_2]$, toluene, 110 °C; (*g*) $[OsCl_3(NO)(PPh_3)_2]$, xylene, 140° C; (*h*) $[OsCl(NO)(PPh_3)_2]$, prepared *in situ* from $[OsCl_3(NO)(PPh_3)_2]$ + L^{Me}_2, xylene, 140 °C, and then excess of olefin, xylene, 140 °C; (*i*) $Ag[BF_4]$, CH_2Cl_2, 25 °C; (*j*) CO, toluene, 25 °C; (*k*) MeI, toluene, 40 °C; (*l*) $PhCH_2Cl$, toluene, 25 °C; (*m*) I_2, CH_2Cl_2, 25 °C; (*n*) Br_2, CH_2Cl_2, 10 °C; (*o*) $[Ni(NO)(PPh_3)_2X]$, toluene, 100 °C tetrakis(carbene) complexes, *trans*-$[MCl(L^{Me})_4(NO)][BF_4]_2$ [M = Ru (5) or Os (7)], which contain the apparently very stable arrangement of four mutually *trans* equatorial L^{Me} ligands {also found in *trans*-$[RuCl_2(L^R)_4]$ (R = Me, Et, or CH_2Ph) and *trans*-$[Ru(CO)Cl(L^{Me})_4Cl]$};[1,11] ^1H and ^{13}C n.m.r. spectra (see below) indicate a very high barrier to rotation around the $Ru-C_{carb.}$ bond.[11] The resistance to carbene-ligand displacement (at >150 °C in air in SMe_2O) is no doubt influenced by (*i*) the strong $M-C_{carb.}$ σ bond,[1,15,16,20] (*ii*) the extensive delocalisation of the dipositive charge on to the L^{Me} ligands[12,21] (see below), and (*iii*) the good π-acceptor character of the NO ligand. Direct tertiary phosphine analogues have not been reported, although monocationic $[RuCl_2(NO)(PR_3)_3]X$ (X = Cl or $[BF_4]$) are known,[3,8] and also related neutral species.[3,5,8] Indeed, among the few known carbeneosmium complexes are the dicationic species[9] *cis*-$[Os(CNMe)_4\{C(NHMe)_2\}_2]X_2$ and *mer*-$[Os(CNMe)_3\{C(NHMe)_2\}_3]X_2$ (X = $[ClO_4]$).



The reaction of (1) with CO in CH_2Cl_2 was unusual in that an oxidation process with NO loss occurred to give in high yield *trans*-$[Ru(CO)Cl(L^{Me})_4]Cl$, instead of the expected (*via* L^{Me} loss) $[Ru(CO)Cl(L^{Me})_2(NO)]$ or $[Ru(CO)(L^{Me})_3(NO)]Cl$. It is likely that CH_2Cl_2 is involved as an oxidant, rather than there being a disproportionation, equation (2). The complex $[Ru(L^{Me})_2(NO)_2]$ has

$$[Ru(L^{Me})_4(NO)]Cl + CO \longrightarrow [Ru(L^{Me})_2(NO)_2] + trans\text{-}[Ru(CO)Cl(L^{Me})_4]Cl + L^{Me}{}_2 \quad (2)$$

has not been unequivocally detected but (*i*) the iron analogue is known,[22] (*ii*) $[Ru(NO)_2(PPh_3)_2]$ exists,[14] and from this $[RuL^{Et}(NO)_2(PPh_3)]$ (14) was formed by reaction with $L^{Et}{}_2$ in hot xylene.

The olefin $L^{CH_2Ph}{}_2$ reacts in a qualitatively different manner from $L^{Me}{}_2$. Although (17) was readily reduced to $[RuCl(NO)(PPh_3)_2]$ (21), excess of olefin only produced the deep blue neutral complex $[RuCl(L^{CH_2Ph})_2(NO)]$ (3), with no further L^{CH_2Ph} incorporation. With (18), reduction did not occur: excess of olefin converted (18) into $[OsCl_2(L^{CH_2Ph})_3(NO)]Cl$ (11) and *trans*-$[OsCl(L^{CH_2Ph})_4(NO)]Cl_2$ (10). Complex (3) is reactive. It readily absorbed CO to give the 18-electron orange-yellow $[Ru(CO)Cl(L^{CH_2Ph})_2(NO)]$ (4) {as does (21), the PPh_3 analogue,[17] forming $[Ru(CO)Cl(NO)(PPh_3)_2]$[4,17]}, but further reaction to form $[Ru(CO)_2(L^{CH_2Ph})_2(NO)]Cl$ was not observed, whereas phosphine analogues are unstable in solution.[1] Complex (3), like (21),[17] but not $[Ru(CO)Cl(NO)(PPh_3)_2]$,[4] underwent oxidative addition of MeI to give $[RuMe(Cl)I(L^{CH_2Ph})_2(NO)]$ (8), but $PhCH_2Cl$ converted (3) into the pale green complex $[RuCl_3(L^{CH_2Ph})_2(NO)]$ (9), with presumably 1,2-diphenylethane as co-product. Complex (3) also readily added I_2 or Br_2 forming $[RuClI_2(L^{CH_2Ph})_2(NO)]$ (12) or $[RuBr_2Cl(L^{CH_2Ph})_2(NO)]$ (13) respectively. Although complex (3) readily reacted with HCl gas, rapid decomposition seemed to occur and a bis(carbene)hydridoruthenium(II) adduct was not characterised; the final product was not, however, the blue starting material (3) (*via* the back reaction), but an uncharacterised buff solid having $\nu(NO)$ at 1 850 cm^{-1}, appropriate for a ruthenium(II) species[23] and $\nu(Ru-H)$ was not detected. This compound is probably *fac*-$[RuCl_3(L^{CH_2Ph})_2(NO)]$, *i.e.* similar in configuration to (24c or d) but different from (24a). This reaction of (3) therefore differs from that of $[RuCl(NO)(PPh_3)_2]$ which was reported to add HCl readily.[17]

The dinitrosyl complex $[Ru(NO)_2(PPh_3)_2]$ (20) does not lose PPh_3 as easily as (21), but prolonged reaction with $L^{Et}{}_2$ in xylene afforded the monocarbene complex $[Ru(L^{Et})(NO)_2(PPh_3)]$ (14); related iron complexes such as $[Fe(CO)L^{Me}(NO)_2]$ and $[Fe(L^{Me})_2(NO)_2]$ have been described previously.[22] The isoelectronic nickel complexes $[Ni(NO)(PPh_3)_2X]$ (X = Br or Cl),[13] however, readily lost both phosphine ligands to give deep blue $[Ni(L^R)_2(NO)X]$ [R = Et, X = Cl (15); R = CH_2Ph, X = Br (16)]. These complexes, although moderately stable when solid {like the isoelectronic $[Ni(CO)_2(L^{Et})_2]$[22]} were slowly oxidised in CH_2Cl_2 solution, accompanied by a blue to orange colour change, presumably to yield square-planar $[Ni(L^R)_2X_2]$ (R = Et, X = Cl; R = CH_2Ph, X = Br).

The rather surprising difference towards carbenemetal complex formation and reducing ability between $L^{Me}{}_2$ and $L^{CH_2Ph}{}_2$ has not been observed so clearly in our previous investigations. Thus an excess of $L^R{}_2$ (R = Me or CH_2Ph) and $[Mo(CO)_6]$, $[RuCl_2(PPh_3)_3]$, *trans*-$[Ir(CO)Cl(PPh_3)_2]$, or $[\{PtCl_2(PEt_3)\}_2]$ yielded *cis*-$[Mo(CO)_4(L^R)_2]$,[15] *trans*-$[RuCl_2(L^R)_4]$,[1] $[Ir(CO)(L^R)_3]Cl$, or *trans*-$[PtCl_2L^R(PEt_3)]$,[24,25] respectively. However, there are sometimes differences in the chemistry between L^R complexes (R = Me or CH_2Ph) most clearly observed in *trans*-$[RuCl_2(L^R)_4]$.[1]

The formation of $[Ru(L^R)_4(NO)]Cl$ for the case of R = Me, but not R = CH_2Ph, is unlikely to be due to differing steric requirements, because *trans*-$[RuCl_2(L^{CH_2Ph})_4]$ is particularly stable,[1] and the covalent radius of Ru^{II} is less than that of Ru^0. Electronic factors which may explain these observations include (*i*) a

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[23] *Cf.* J. H. Enemark and R. D. Feltham, *Co-ordination Chem. Rev.*, 1974, **13**, 339 and refs. therein.

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stronger Ru–$C_{carb.}$ σ bond for L^{CH_2Ph},[1] and (*ii*) a decreased tendency towards Cl^- displacement.[12] The particularly unexpected (for L^{Me}_2 rather than $L^{CH_2Ph}_2$) result is the formation of (1).

TABLE 2

Hydrogen-1 n.m.r. spectroscopic data for carbenenitrosyl-ruthenium, -osmium, and -nickel complexes [a]

Complex	Solvent	N–CH_2CH_2–N	N–CH_2–	N–( )–CH_3
(1) [b]	CH_2Cl_2	6.50		7.30
(2) [c]				
(3)	CD_2Cl_2	6.25	4.55	
(4)	C_6D_6	7.23	5.15 (q) [d]	
(5) [e]	$S(CD_3)_2O$	6.30 (br)		6.95, 7.10
(6) [e]	$S(CD_3)_2O$	6.32 (br)		6.93, 7.08
(7)	$S(CD_3)_2O$	6.20 (br m)		6.93, 7.07
(8)	$CDCl_3$	6.70	4.8 (br)	*f*
(9)	CD_2Cl_2	6.75	5.1 (q) [d]	
(10)	$S(CD_3)_2O$	6.1 (br m)	4.2 (d), 5.3 (d), 5.0 (br)	
(11)	$S(CD_3)_2O$	6.1—6.6 (br m)	[4.1—5.4 (m)]	
(12) [g]	$S(CD_3)_2O$	6.3 (br m) [h]	4.85 (br m) [h]	
(13) [g]	$S(CD_3)_2O$	6.4 (br m) [h]	4.75 (br m) [h]	
(14)	$CDCl_3$	5.9—6.6 (m)	5.9—6.6 (m)	8.9 (t), 9.0 (t)
(15)	C_6D_6	7.1	6.35 (q)	9.0 (t)
(16)	$CDCl_3$	6.60	5.00	

[a] All resonances quoted in τ relative to $SiMe_4$ (τ 10) or to corrected solvent resonance at 35 °C. All the peaks were singlets unless stated; d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. [b] Complete decomposition after *ca.* 30 min, 35 °C; resulting signals indistinct and unassigned. Unidentified orange-brown complex, probably $[Ru(L^{Me})_2(NO)_2]$, also isolated from reaction giving (1), exhibits resonances at τ 6.52 (NCH_2CH_2N) and 7.05 (N–CH_3). Spectrum unchanged at −90 °C. [c] Complete decomposition in CH_2Cl_2 within 5 min above −90 °C. [d] AB pattern; the value quoted is the mid-point of the inner components. [e] Spectrum unchanged at 150 °C. [f] Ru–CH_3, τ 8.06. [g] Spectrum recorded at 100 °C. [h] Mid-point of multiplet.

The difference in reducing properties, *e.g.* $[MCl_3(NO)(PPh_3)_2]$ [M = Ru (17) or Os (18)] are each reduced by L^{Me}_2 but only the former by $L^{CH_2Ph}_2$, may be traced to the first vertical ionisation potential of the olefins: that of L^{Me}_2 is 6.0 eV,[26] and for $L^{CH_2Ph}_2$ is estimated as *ca.* 6.5 eV (the complex is not readily vaporised).[27,†]

TABLE 3

Selected ^{13}C n.m.r. spectroscopic data for carbenenitrosyl-ruthenium, -osmium, and -nickel complexes [a]

Complex	Solvent	$C_{carb.}$	N–CH_2CH_2–N	N–CH_3	N–CH_2–( )
(1) [b]	CD_2Cl_2	220.4	51.7	37.9	
(3)	CD_2Cl_2	216.2	48.5		55.9
(4)	CD_2Cl_2	207.3 (240.7) [c]	48.8		55.0
(5)	$S(CD_3)_2O$	190.5	52.3, 51.4	38.2, 37.5	
(7)	$S(CD_3)_2O$	177.6	52.0, 51.1	37.2, 38.0	
(10)	$S(CD_3)_2O$	180.2	49.6, 49.4		56.1, 54.1
(11)	$S(CD_3)_2O$	179.6,[d] 174.9 [e]	49.1 [f]		55.0, 53.8[f]
(15)	CD_2Cl_2	225.6	48.8		44.7

[a] All the complexes were run as saturated solutions in 8- or 10-mm tubes at 25 °C, using a 1-s repetition rate and a sweep width of 6 250 Hz. Resonances are quoted in p.p.m. relative to $SiMe_4$ (0 p.p.m.) or the corrected solvent resonance. [b] Rapid decomposition occurs (*ca.* 30 min, 25 °C). [c] δ[*C*(CO)]. [d] Two mutually *trans* L^{CH_2Ph}. [e] One *cis*-L^{CH_2Ph}. [f] Signal broad and unresolved.

Spectroscopic Properties.—The crimson complex $[Ru(L^{Me})_4(NO)]Cl$ (1) exhibited a temperature-invariant (−95 to +35 °C) ^1H n.m.r. spectrum (Table 2) consisting of two sharp singlets, N–CH_3 and ring CH_2, and similarly ^{13}C n.m.r. (Table 3) indicated equivalence of all the L^{Me} ligands. These observations are consistent with four mutually *trans* equatorially arranged carbene ligands in a complex of s.b.p.) square-based pyramidal) geometry (22), with restricted rotation about the $RuC_{carb.}$ bonds, but facile rotation about the Ru–NO bond, although if complex (1) is considered to contain Ru^0 (*i.e.* d^8), t.b.p. (trigonal-bipyramidal) geometry might have been expected.[23] The exceptionally low value of ν(NO) (Table 4) [thought to be at *ca.* 1 470 cm^{-1} for (1) and (2)] is suggestive of a bent nitrosyl ligand with much of the electron density (from the strong σ-donating L^{Me} ligands) in the π*-NO molecular orbital (m.o.),‡,§ and s.b.p. geometry was predicted for d^8 five-co-ordinate complexes containing bent terminal NO.[23] Low values of ν(NO) are observed for s.b.p. $[IrCl_2(NO)(PPh_3)_2]$ at 1 560 cm^{-1},[28] and $[IrMeI(NO)(PPh_3)_2]$ at 1 525 cm^{-1},[29] which contain (*i*) axial bent NO ligands but (*ii*) weaker neutral σ-donor ligands than L^{Me}. The presence of the

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† Throughout this paper: 1 eV ≃ 1.60 × 10^{-19} J.

‡ For a detailed m.o. treatment and discussion of the geometries associated with a terminal and bent co-ordinated NO in a five-co-ordinate, formally d^8, environment see ref. 23.

§ *Note added in proof:* Passage of CO gas for 30 min through a warm CH_2Cl_2 solution of $[RuCl(L^{CH_2Ph})_2(NO)]$ (3) appears to give a yellow-brown structural isomer of the yellow–orange $[Ru(CO)Cl(L^{CH_2Ph})_2(NO)]$ (4) containing a *linear* NO ligand and having a *t.b.p. geometry* [ν(CO 1 822, ν(NO) 1 692 cm^{-1}; *cf.* the *s.b.p., bent* NO (4): ν(CO) 1 910, ν(NO) 1 540 cm^{-1}].

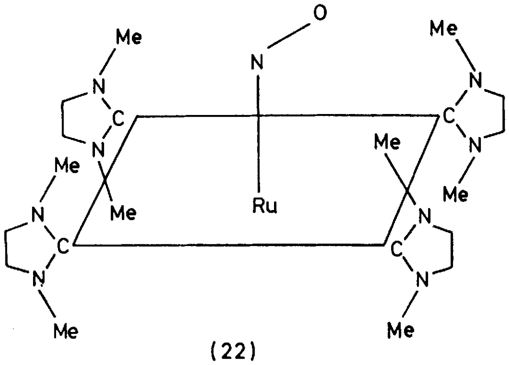
[26] B. Çetinkaya, G. H. King, S. S. Krishnamurthy, M. F. Lappert, and J. B. Pedley, *Chem. Comm.*, 1971, 1870.

[27] A. J. Rogers, unpublished work.

[28] J. A. Ibers and D. M. P. Mingos, *Inorg. Chem.*, 1971, **10**, 1035.

[29] J. A. Ibers, D. M. P. Mingos, and W. T. Robinson, *J. Chem. Soc. (A)*, 1971, 2146.

four strongly σ-donating carbene ligands could also be expected significantly to lower ν(NO), whether linear or bent. Comparison of ν(NO) in a complex containing both terminal and bent NO ligands[30] suggests that $\Delta\nu$(NO) is *ca.* 200 cm^{-1}; therefore, whereas ν(NO) for $[RuCl(L^{CH_2Ph})_2(NO)]$ is at 1 697 cm^{-1}, for $[Ru(L^{Me})_4(NO)]Cl$, which contains four rather than two donors of high σ-donor : π-acceptor ratio, ν(NO) would be predicted to lie between 1 400 and 1 500 cm^{-1}. For t.b.p. $[Ru(NO)(dppe)_2]^+$ (tertiary phosphine *P*-donors have a lower σ-donor : π-acceptor ratio than a carbene *C*-donor), ν(NO) (linear)[31] is at 1 673 cm^{-1},[8] and for $K_4[Mo(CN)_5(NO)]$ ν(NO) is at 1 455 cm^{-1},[32] the low value here being consistent with the tetra-anionic nature of the complex.



(22)

TABLE 4

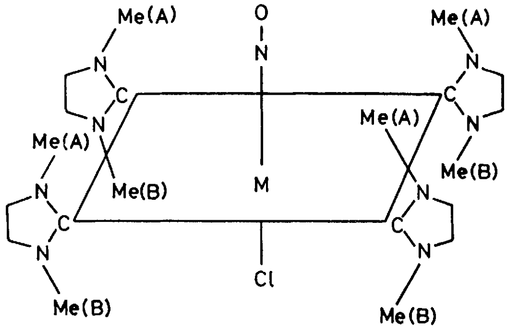
Infrared spectroscopic data for carbenenitrosyl-ruthenium, -osmium, and -nickel complexes

Complex	ν(NO) [a]	$\nu(CN_2)$ [a]	Others
(1)	*ca.* 1 470s, br [b]	1 500s	
(2)	*ca.* 1 465s, br [b]	1 501s	
(3)	1 692s	1 500s	312m [c]
(4)	1 540s [d]	1 502m—s	
(5)	1 835s	1 535s, 1 515 (sh)	330w [c]
(6)	1 835s	1 535s, 1 515 (sh)	330w [c]
(7)	1 818s	1 535s, 1 515 (sh)	330m—w [e]
(8)	1 807s	1 492m—s	310m—w [c]
(9)	1 780s	1 506m—s	310m—w [c]
(10)	1 813s	1 501s	325m—w [e]
(11)	1 816s	1 500s	325w, 280w [e]
(12)	1 851s	1 498m	322w
(13)	1 847s	1 498m	328w
(14)	1 620s, 1 575s	1 482m	
(15)	1 660s	1 500s	
(16)	1 695s	1 503s	

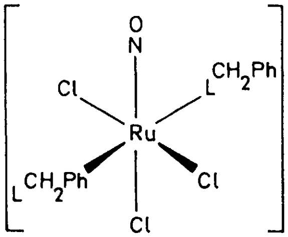
[a] Obtained from a dilute Nujol mull between CsI plates. [b] ν(NO) not unambiguously assigned because of proximity to $\nu(CN_2)$ and δ(C–H) absorptions; the band at *ca.* 1 470 cm^{-1} disappears on aerial oxidation of (1) or (2). Values quoted from CH_2Cl_2 solution for (1) and Nujol mull for (2). [c] ν(Ru–Cl). [d] In thf solution; ν(CO) at 1 910 cm^{-1}. [e] ν(Os–Cl).

The *trans*-$[RuCl(L^{Me})_4(NO)]^{2+}$ and *trans*-$[OsCl(L^{Me})_4(NO)]^{2+}$ dications, (23), showed two distinct CH_3 signals (A and B) up to >150 °C (in SMe_2O). A similar result was also observed for the N–CH_2Ph protons in *trans*-$[OsCl(L^{CH_2Ph})_4(NO)]^{2+}$; these complexes thus exhibit extremely high (>25 kcal mol^{-1}) $\Delta G^{\ddagger}$ barriers to rotation about M–C$_{carb.}$ (M = Ru or Os). We consider this to originate from intramolecular steric hindrance, rather than any d_π–p_π M–C$_{carb.}$ interaction,[1,11,15] which does not appear to be of importance in complexes containing L^R (R = Me, Et, or CH_2Ph) ligands.

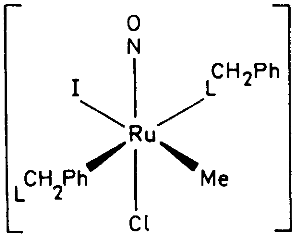
The low values of ν(NO) in $[RuMe(Cl)I(L^{CH_2Ph})_2(NO)]$ (8) (1 807 cm^{-1}) and $[RuCl_3(L^{CH_2Ph})_2(NO)]$ (9) (1 780 cm^{-1}) compared to *ca.* 1 850 cm^{-1} in $[RuClI_2(L^{CH_2Ph})_2(NO)]$ (12) and $[RuBr_2Cl(L^{CH_2Ph})_2(NO)]$ (13) suggest different ligand configurations in the two sets of complexes. The *mer* isomer has generally been observed in tertiary phosphine analogues,[3] being the thermodynamic product, the *fac* isomer rearranging in solution.[8] Here complexes (8) and (9) were recovered unchanged from solution and, although the low values of ν(NO) would be explicable by considering an L^{CH_2Ph} ligand *trans* to NO, ^{1}H n.m.r. spectroscopy showed equivalence of the two carbene fragments; these two complexes are therefore considered to have the *mer* stereochemistries (24a) and (24b) respectively. Conversely the ^{1}H n.m.r. spectra of



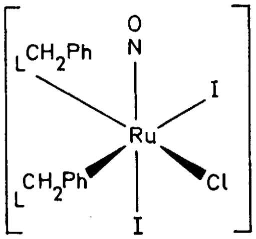
(23) M = Ru or Os



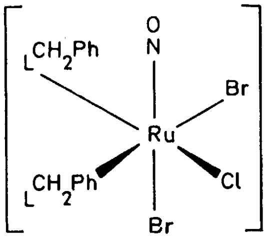
(24a)



(24b)



(24c)



(24d)

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[30] C. G. Pierpont, D. G. Van Derveer, W. Durland, and R. Eisenberg, *J. Amer. Chem. Soc.*, 1970, **92**, 4760.

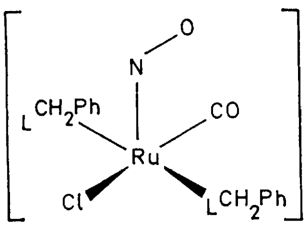
[31] C. G. Pierpont, A. Pucci, and R. Eisenberg, *J. Amer. Chem. Soc.*, 1971, **93**, 3050.

[32] R. F. Riley and L. Ho, *J. Inorg. Nuclear Chem.*, 1962, **24**, 1121.

(12) and (13) [these complexes are far less soluble in $CDCl_3$ or CD_2Cl_2 than (8) or (9), as expected for a *fac* isomer] were more complicated and this suggests inequivalence of the carbene ligands; we therefore propose the configurations shown in (24c) and (24d). Here I^- or Br^- is *trans* to NO, even though Cl^- *trans* to NO has previously been thought to be preferred because of its lower *trans* influence.[26]

The complex $[Ru(CO)Cl(L^{CH_2Ph})_2(NO)]$ (4) has a low value of ν(NO), at 1 540 cm^{-1}, characteristic of a bent NO group and may be compared with the value for the PPh_3 analogue at 1 592 cm^{-1}.[4] The lower value in the former does not necessarily imply a greater degree of bending in the Ru–N–O group; the decrease of *ca.* 50 cm^{-1} would be expected because of the differing electronic properties of L^{CH_2Ph} and PPh_3. Although $[Ru(CO)I(NO)(PPh_3)_2]$ has ν(NO) at 1 642 cm^{-1}, it has been shown[4] to have t.b.p. geometry and an almost linear Ru–NO group, and the linearity and geometry of these complexes appear to be dependent on the anionic ligand; NO in the hydroxo-complex $[Ru(CO)(NO)(OH)(PPh_3)_2]$ was considered to be bent, with ν(NO) at 1 555 cm^{-1}.[4] From the available spectroscopic evidence complex (4) most likely approximates to the idealised s.b.p. structure shown in (25).

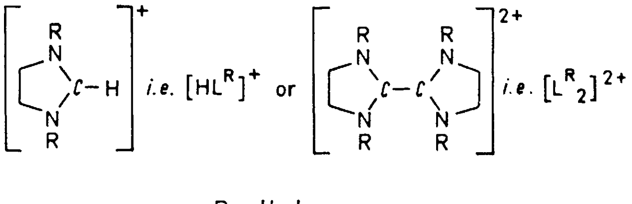
It is of interest to compare the values of the carbonyl and nitrosyl stretching frequencies in these pairs of complexes: ν(CO) at 1 910 cm^{-1} and ν(NO) at 1 540 cm^{-1} in (4); but ν(CO) at 1 925 cm^{-1} and ν(NO) at 1 592 cm^{-1} in $[Ru(CO)Cl(NO)(PPh_3)_2]$.[4] These values suggest that the excess of electron density on the metal (because of the greater σ-donor : π-acceptor ratio of L^R compared to the PPh_3 ligand) is preferentially removed by NO rather than the CO ligand. This is consistent with the suggestion that NO is the best π-accepting ligand.[33] Similar low ν(NO) shifts were observed between $[RuCl(NO)(PPh_3)_2]$ and $[RuCl(L^{CH_2Ph})_2(NO)]$ (3) (that of the former being at 1 740 cm^{-1},* the latter at 1 692 cm^{-1}), $[Ru(NO)_2(PPh_3)_2]$ [7,14] and $[RuL^{Et}(NO)_2(PPh_3)]$ (14), (1 665 and 1 615, and 1 620 and 1 575 cm^{-1}, respectively), and $[NiCl(NO)(PPh_3)_2]$ [13] and $[NiCl(L^{Et})_2(NO)]$ (15) (*ca.* 1 735 and 1 660 cm^{-1}, respectively).



(25)

There are several trends in the ^{13}C n.m.r. spectral data (Table 3) with respect to a high-field shift of the $C_{carb.}$ resonance. (*i*) In the series (1), (3), and (4), $\delta(C_{carb.})$ is at 220.4, 216.2, and 207.3 p.p.m. respectively. The upfield shift corresponds to (*a*) a reduction in the number of L^R ligands and (*b*) the introduction of a second good π-acceptor ligand, CO (*i.e.* reducing the negative charge on the metal) whilst the formal oxidation state of the metal remains constant. It must be noted, however, that within this series the metal environment does change (*i.e.* charge on complex, co-ordination number, and geometry), but we consider that (*a*) and (*b*) are the principal reasons for the observed shift in $\delta(C_{carb.})$. (*ii*) Replacing a lighter by a heavier metal, the complex type remaining constant, as in $[MCl(L^{Me})_4(NO)][BF_4]_2$ [5; M = Ru, $\delta(C_{carb.})$ 190.5 p.p.m.] and [7; M = Os, $\delta(C_{carb.})$ 177.5 p.p.m.] causes an upfield shift (see also ref. 34). (*iii*) Changing, in a related series, from a neutral to a mono- and then a di-cationic complex, the number of carbene ligands and stereochemistry remaining constant, results in a constant upfield shift of $\delta(C_{carb.})$.

A series (*iii*) is best illustrated by comparison of *trans*-$[RuCl_2(L^{Et})_4]$ [neutral, $\delta(C_{carb.})$ 226 p.p.m.],[1,11] *trans*-$[Ru(CO)Cl(L^{Me})_4]Cl$ [monocationic, $\delta(C_{carb.})$ 208 p.p.m.],[1,11] and *trans*-$[RuCl(L^{Me})_4(NO)][BF_4]_2$ [dicationic, $\delta(C_{carb.})$ 190 p.p.m.], *i.e.* there is an 18 p.p.m. upfield shift for each positive charge per four similar carbene ligands. For the 'isolated' related carbonium (amidinium) ions (see above), a value of 154 p.p.m. would thus be predicted for *C*: in practice values of 160 and 148 p.p.m. were observed[15,35] (average 154 p.p.m.). These data reinforce the suggestion that the positive and dipositive charges in the above *trans*-tetrakis(carbene) complexes are significantly delocalised on to the carbene ligands. The values of $\nu(CN_2)$ are also informative: they increase in the order 1 485 (neutral),[1] 1 510 (monocationic),[1] and 1 535 cm^{-1} (dicationic). In complexes (5) and (7) the stereochemically rigid environment is further demonstrated by the observation of doublet signals for the inequivalent N–CH_3 groups and the ring methylene *C* atoms, whereas the four carbene carbon atoms were observed as a sharp singlet {as in *trans*-$[Ru(CO)Cl(L^{Me})_4]Cl$ [1,11]}.



R = alkyl

Complex (1) also showed a single $C_{carb.}$ resonance at 220 p.p.m., but only one set of N-CH_3 and ring CH_2 signals, in accord with the ^1H n.m.r. spectrum. The osmium analogue (2) was too unstable in solution for a comparative spectrum to be recorded. The values of

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* This work (dilute Nujol mull between CsI plates).

[33] F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' 2nd edn., Wiley, New York, 1967, p. 538.

[34] D. J. Cardin, B. Çetinkaya, E. Çetinkaya, M. F. Lappert, E. W. Randall, and E. Rosenberg, *J.C.S. Dalton*, 1973, 1982.

[35] M. F. Lappert and P. L. Pye, *Proc. 2nd Internat. Molybdenum Conf.*, Oxford, September 1976, p. 101; *J. Less-Common Metals*, 1977, **54**, 191.

$C_{carb.}$ for the osmium(II) complexes (7), (10), and (11) are numerically lower (*i.e.* $C_{carb.}$ is more shielded) than for the related ruthenium(II) species (5); this is generally the observed trend for the heavier metal [*e.g.* a comparison of $\delta(C_{carb.})$ in complexes of Mo^0 (ref. 15) and W^0,[16] or Pd^{II} (ref. 34) and Pt^{II} (ref. 34)] and is also observed for the CO ligands in the series *cis*-$[M(CO)_2Cl_2(PR_3)_2]$ (*e.g.* M = Ru or Os).[36]

$C_{carb.}$ for L^{CH_2Ph} is at slightly lower field than $C_{carb.}$ for L^{Me} in the pair (7) and (10): this is a trend also observed between the pairs $[Mo(CO)_5L^R]$ (R = Me and CH_2Ph),[15] and *trans*-$[RuCl_2(L^R)_4]$ (R = Et and CH_2Ph),[1] and may be due to the small $-I$ effect of a Ph compared to an H group: it is also noted that $C_{carb.}$ for L^{Et} is generally at a slightly higher field than $C_{carb.}$ for L^{Me}, the $+I$ effect of Me being greater than that of H.

EXPERIMENTAL

General procedures used have been described previously.[1,15,16,18] The starting materials $[RuCl_3(NO)(PPh_3)_2]$,[5] $[OsCl_3(NO)(PPh_3)_2]$,[2] $[Ru(NO)_2(PPh_3)_2]$,[14] and $[Ni(NO)(PPh_3)_2X]$[13] were prepared from $RuCl_3\cdot nH_2O$, $[NH_4]_2[OsBr_6]$, and $[Ni(PPh_3)_2X_2]$ by literature methods. The electron-rich olefins $L^{Me}{}_2$ and $L^{Et}{}_2$ were prepared *via* the acetal $Me_2NCH(OMe)_2$ and the relevant 1,2-diaminoethane $RHNCH_2CH_2NHR$ by the prescribed procedure.[37] A variation of that described for $L^{CH_2Ph}{}_2$ is given here.

$[Ru(L^{Me})_4(NO)]Cl$.—To a solution of $[RuCl_3(NO)(PPh_3)_2]$ (0.35 g, 0.5 mmol) in toluene (20 cm^3) was added bi(1,3-dimethylimidazolidin-2-ylidene) ($L^{Me}{}_2$) (0.30 g, 2.5 mmol) and the mixture heated under reflux (10 min). The initial dark green colour changed to orange-brown and then a crimson microcrystalline solid precipitated (10 min). This was removed by filtration of the hot solution, washed with OEt_2 (5 × 10 cm^3), and dried to afford *tetrakis*(1,3-*dimethylimidazolidin*-2-*ylidene*)*nitrosylruthenium chloride* (0.22 g, 80%).

$[Os(L^{Me})_4(NO)]Cl$.—To a suspension of $[OsCl_3(NO)(PPh_3)_2]$ (0.43 g, 0.5 mmol) in xylene (20 cm^3) was added $L^{Me}{}_2$ (0.20 g, 1.0 mmol) and the mixture heated under reflux (1 h) to give a brown-orange solution and a pale brown precipitate. The mixture was filtered, an excess of olefin (0.40 g, 2.0 mmol) added, and the mixture again heated under reflux to deposit slowly a purple precipitate (10 min). This was removed by filtration, washed with OEt_2 (5 × 10 cm^3), and dried *in vacuo* to afford *tetrakis*(1,3-*dimethylimidazolidin*-2-*ylidene*)*nitrosylosmium chloride* (0.20 g, 65%).

$[RuCl(NO)(PPh_3)_2]$ via *Reduction using an Electron-rich Olefin*.—To a suspension of $[RuCl_3(NO)(PPh_3)_2]$ (0.76 g, 1.0 mmol) in toluene (20 cm^3) was added tetrapyrrolidinylethylene (tpen) (0.32 g, 1.1 mol). The yellow suspension was almost immediately replaced by a dark green solution and a dark solid. The mixture was heated (110 °C, 10 min) to ensure dissolution of the green product and filtered while hot. The residue was extracted with hot toluene (100 °C, 10 cm^3), filtered, and the filtrates combined (leaving an off-white residue). Addition of hexane (15 cm^3) to the combined filtrates and cooling (−30 °C, 12 h) afforded dark green microcrystals of chloronitrosylbis(triphenylphosphine)ruthenium (0.67 g, 95%). It is to be noted that, although the reduction is readily accomplished using $L^{Me}{}_2$, $L^{Et}{}_2$, or $L^{CH_2Ph}{}_2$ (but not $L^{aryl}{}_2$), in order to avoid the possibility of any further reaction of olefin with the reduced ruthenium complex it is preferable to use a non-carbene-metal complex-forming olefin, such as tetrakis(dimethylamino)ethylene (tden) or the more easily prepared tpen. {It is considered likely that $[OsCl(NO)(PPh_3)_2]$ could be isolated by reducing $[OsCl_3(NO)(PPh_3)_2]$ with tden, although tpen does not react.}

$[RuCl(L^{CH_2Ph})_2(NO)]$.—To a solution of $[RuCl(NO)(PPh_3)_2]$ (0.35 g, 0.5 mmol) in xylene (30 cm^3) was added bi(1,3-dibenzylimidazolidin-2-ylidene) ($L^{CH_2Ph}{}_2$) (1.0 g, 2.0 mmol) and the mixture heated (140 °C, 4 h). The initial green solution slowly became grey and on cooling small deep blue crystals of the product *chlorobis*(1,3-*dibenzylimidazolidin*-2-*ylidene*)*nitrosylruthenium* (0.31 g, 95%) were deposited. These were removed by filtration, washed with OEt_2 (3 × 10 cm^3), and dried *in vacuo*.

trans-$[RuCl(L^{Me})_4(NO)]X_2$.—(*i*) X = $[BF_4]$. To a stirred solution of $[Ru(L^{Me})_4(NO)]Cl$ (0.23 g, 0.40 mmol) in CH_2Cl_2 (15 cm^3) was added solid $Ag[BF_4]$ (0.20 g, 1.0 mmol) in portions. Silver was deposited and the crimson solution became yellow-brown. After complete addition, the mixture was filtered and OEt_2 (10 cm^3) added slowly to cause precipitation of the pale yellow microcrystalline product trans-*chlorotetrakis*(1,3-*dimethylimidazolidin*-2-*ylidene*)*nitrosylruthenium bis*(*tetrafluoroborate*) (0.23 g, 80%).

(*ii*) X = $[ClO_4]$. A similar procedure to that described above was followed, but use of $Ag[ClO_4]$ afforded the *diperchlorate* salt as a yellow powder.

trans-$[OsCl(L^{Me})_4(NO)][BF_4]_2$.—To a cooled solution of $[Os(L^{Me})_4(NO)]Cl$ (0.16 g, 0.25 mmol) in CH_2Cl_2 (10 cm^3, −45 °C) was added $Ag[BF_4]$ (0.10 g, 0.50 mmol) in portions. Silver was deposited and the solution became yellow-green. The mixture was filtered and slow addition of OEt_2 (10 cm^3) afforded pale green-yellow microcrystals of trans-*chlorotetrakis*(1,3-*dimethylimidazolidin*-2-*ylidene*)*osmium bis*(*tetrafluoroborate*) (0.15 g, 75%).

$[Ru(CO)Cl(L^{CH_2Ph})_2(NO)]$.—Carbon monoxide was bubbled through a stirred suspension of $[RuCl(L^{CH_2Ph})_2(NO)]$ (0.33 g, 0.5 mmol) in warm toluene (15 cm^3, 50 °C) until the blue solid disappeared and an orange solution formed. OEt_2 (5 cm^3) was added and the mixture cooled (−30 °C, 24 h) to afford orange crystals of *carbonylchlorobis*(1,3-*dibenzylimidazolidin*-2-*ylidene*)*nitrosylruthenium*.

$[RuMe(Cl)I(L^{CH_2Ph})_2(NO)]$.—An excess of methyl iodide (1 cm^3) was added to a stirred suspension of $[RuCl(L^{CH_2Ph})_2(NO)]$ (0.16 g, 0.25 mmol) in toluene (5 cm^3) and the mixture gently warmed (50 °C, 5 min). The blue solid slowly disappeared and the solution became orange-brown. Hexane (*ca.* 5 cm^3) was slowly added to cause precipitation of orange-brown microcrystals of *chlorobis*(1,3-*dibenzylimidazolidin*-2-*ylidene*)*iodo*(*methyl*)*nitrosylruthenium* (0.16 g, 80%).

$[RuCl_3(L^{CH_2Ph})_2(NO)]$.—To a stirred solution of $[RuCl(L^{CH_2Ph})_2(NO)]$ (0.16 g, 0.25 mmol) in CH_2Cl_2 (5 cm^3) was added an excess of benzyl chloride (2 cm^3). On warming (40 °C) the blue colour rapidly became pale green and addition of OEt_2 (10 cm^3) precipitated a pale green solid, which was recrystallised from CH_2Cl_2–OEt_2 (−30 °C, 24 h) to afford pale green microcrystals of *trichlorobis*(1,3-*dibenzylimidazolidin*-2-*ylidene*)*nitrosylruthenium* (0.12 g, 66%).

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[36] D. F. Gill, B. E. Mann, and B. L. Shaw, *J.C.S. Dalton*, 1973, 311.

[37] H. E. Winberg, U.S.P. 3,239,519(1966); *Chem. Abs.*, 1966, **64**, 15854h.

$[RuClI_2(L^{CH_2Ph})_2(NO)]$.—To a rapidly stirred solution of $[RuCl(L^{CH_2Ph})_2(NO)]$ (0.16 g, 0.25 mmol) in CH_2Cl_2 (2 cm^3) was added di-iodine (0.07 g, 0.27 mmol). The blue solution rapidly became red-orange. Diethyl ether (*ca.* 10 cm^3) was added slowly to cause precipitation of a microcrystalline product, which was recrystallised from CH_2Cl_2–OEt_2 (−30 °C, 24 h) to yield dark orange crystals of *chlorobis*(1,3-*dibenzylimidazolidin*-2-*ylidene*)*di-iodonitrosylruthenium* (0.2 g, 90%).

$[RuBr_2Cl(L^{CH_2Ph})_2(NO)]$.—To a solution of $[RuCl(NO)(PPh_3)_2]$ (0.16 g, 0.25 mmol) in CH_2Cl_2 (5 cm^3) was added dropwise dibromine (0.04 g, 0.28 mmol) in CH_2Cl_2 (2 cm^3). The blue solution became orange and dropwise addition of OEt_2 (*ca.* 5 cm^3) caused precipitation of an orange-brown solid. This was removed by filtration and recrystallised from CH_2Cl_2–OEt_2 (−30 °C, 6 h) to afford small orange-brown crystals of *dibromochlorobis*(1,3-*dibenzylimidazolidin*-2-*ylidene*)*nitrosylruthenium* (0.16 g, 75%).

$[OsCl_2(L^{CH_2Ph})_3(NO)]Cl$ *and trans*-$[OsCl(L^{CH_2Ph})_4(NO)]Cl_2$.—To a suspension of $[OsCl_3(NO)(PPh_3)_2]$ (0.95 g, 1.0 mmol) in xylene (30 cm^3) was added $L^{CH_2Ph}{}_2$ (1.5 g, 3.0 mmol) and the mixture heated under reflux (1 h). The orange suspension became pale yellow and was removed by filtration. The residue was extracted with CH_2Cl_2 (2 × 15 cm^3) to give a pale orange solution and undissolved yellow solid. The solution was filtered and OEt_2 was carefully layered on to the filtrate, and was left undisturbed (25 °C, 72 h) to afford orange-yellow microcrystals of *dichlorotris*(1,3-*dibenzylimidazolidin*-2-*ylidene*)*nitrosylosmium chloride* (0.29 g, 27%). The original undissolved solid was washed with acetone (1 × 10 cm^3), ethanol (1 × 10 cm^3), and OEt_2 (5 × 10 cm^3), and dried *in vacuo* to give pale yellow trans-*chlorotetrakis*(1,3-*dibenzylimidazolidin*-2-*ylidene*)*nitrosylosmium dichloride* (0.90 g. 68%).

$[RuL^{Et}(NO)_2(PPh_3)]$.—To a suspension of $[Ru(NO)_2(PPh_3)_2]$ (0.31 g, 0.45 mmol) in $C_6H_{11}Me$ (5 cm^3) and toluene (5 cm^3) was added bi(1,3-diethylimidazolidin-2-ylidene) ($L^{Et}{}_2$) (0.12 g, 0.48 mmol). The mixture was heated (100 °C, 5 h). On cooling (30 °C) a solid precipitated (starting material) which was removed by filtration. Cooling the filtrate (−20 °C, 72 h) afforded brown-purple crystals of (1,3-*diethylimidazolidin*-2-*ylidene*)*dinitrosyl*(*triphenylphosphine*)*ruthenium* (0.08 g, 32%).

$[NiCl(L^{Et})_2(NO)]$.—To $[NiCl(NO)(PPh_3)_2]$ (0.61 g, 0.93 mmol) in toluene (15 cm^3) was added $L^{Et}{}_2$ (0.25 g, 1.0 mmol) and the mixture heated (110 °C, 2 h) to form a deep blue solution. This was cooled (0 °C) and filtered. Diethyl ether (15 cm^3) was added to the filtrate which was then further cooled (−30 °C, 36 h) to afford *chlorobis*(1,3-*diethylimidazolidin*-2-*ylidene*)*nitrosylnickel* (0.30 g, 85%) as deep blue crystals which were removed by filtration, washed with cold OEt_2 (0 °C, 3 × 5 cm^3), and dried *in vacuo*. Similarly prepared from $[NiBr(NO)(PPh_3)_2]$ and $L^{CH_2Ph}{}_2$ was *bromobis*-(1,3-*dibenzylimidazolidin*-2-*ylidene*)*nitrosylnickel*.

Reaction of $[Ru(L^{Me})_4(NO)]Cl$ *with* CO.—Carbon monoxide was bubbled through a solution of $[Ru(L^{Me})_4(NO)]Cl$ (0.11 g, 0.2 mmol) in CH_2Cl_2 (5 cm^3). The initial crimson colour of the solution was rapidly discharged and became pale yellow. Diethyl ether (5 cm^3) was slowly added to precipitate an off-white microcrystalline solid, which was removed by filtration, washed with OEt_2 (2 × 5 cm^3), dried, and identified by i.r. and ^1H n.m.r. spectroscopy as *trans*-carbonylchlorotetrakis(1,3-dimethylimidazolidin-2-ylidene)ruthenium chloride (0.10 g, 90%) by comparison with an authentic sample.[1]

Synthesis of Bi(1,3-*dibenzylimidazolidin*-2-*ylidene*) ($L^{CH_2Ph}{}_2$).—A mixture of 1,2-bis(benzylamino)ethane (12.0 g, 0.05 mol) and dimethylformamide dimethyl acetal (7.0 g, 0.06 mol) in methylcyclohexane (50 cm^3) was heated under reflux under dinitrogen, using a hot-water condenser the top of which was fitted with a T piece to allow the escape of dimethylamine and methanol into a cooled trap (−78 °C). When the theoretical quantity of $NHMe_2$ and MeOH had been collected (*ca.* 3—6 h reaction time) the reaction mixture was allowed to cool slowly to room temperature whereupon crystals of the product were deposited. After further cooling (−30 °C, 4 h) the crystals were removed by filtration, washed with cold OEt_2 (−10 °C, 5 × 10 cm^3) and hexane (2 × 10 cm^3), and dried *in vacuo* to afford bi(1,3-dibenzylimidazolidin-2-ylidene) (11.5 g, 92%) as a pale cream crystalline material.

[7/1574 *Received, 5th September,* 1977]