Carbene Complexes. Part 13.[1] The Synthesis and Characterisation of Secondary Carbene Complexes of Vanadium(I), Chromium(0), Molybdenum(0), Tungsten(0), Manganese(I), Rhenium(I), Iron(0), Ruthenium(II), Cobalt(I), Iridium(III), and Platinum(IV), and Hydridorhodium(III) †

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(Chloromethylene)dimethylammonium chloride [NMe$_2$(CHCl)]Cl (or its dibromo-analogue) is a convenient source of secondary carbenemetal complexes [M{CH(NMe$_2$)}L$_n$]. As well as three-fragment oxidative addition to d^8 metal complexes (Ru^0, Ir^I, or Pt^{II}) to give d^6 adducts, two other procedures have been developed: salt elimination from a transition-metallate dianion precursor (V^{-I}, Cr^{-II}, Mo^{-II}, W^{-II}, or Fe^{-II}), and salt elimination with concomitant oxidative addition using a transition-metallate monoanion precursor (Mo^0, W^0, Mn^{-I}, Re^{-I}, or Co^{-I}). The carbenerhodium(III) complex [{Rh[CH(NMe$_2$)](CO)Cl$_3$}$_2$] reacts with PPh$_3$ in ethanol to yield the hydridocarbene complex [Rh{CH(NMe$_2$)}Cl$_2$H(PR$_3$)$_2$] (R = Ph) from which analogues (R$_3$ = Et$_3$ or Me$_2$Ph) are accessible. Infrared and ^{1}H or ^{13}C n.m.r. spectra have been used to characterise the 23 new complexes and establish their stereochemistry.

THIS paper is mainly concerned with the interaction of (chloromethylene)dimethylammonium chloride [NMe$_2$-(CHCl)]Cl and some transition-metal substrates, and the characterisation of the derived secondary carbene-metal complexes. In this way, three general methods

RESULTS AND DISCUSSION

(*i*) *Three-fragment Oxidative Addition.*—This is defined in its general form by equation (1). The term ' three-fragment oxidative addition ' was proposed to encompass two-electron oxidations in which the transition-metal
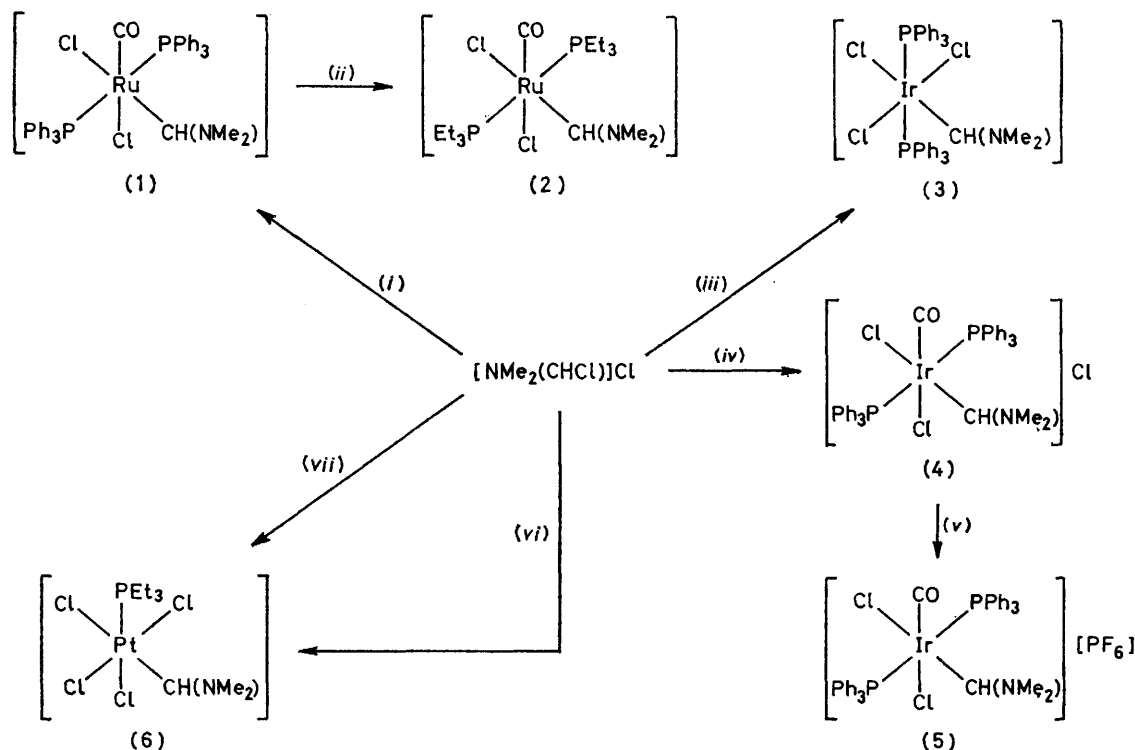
SCHEME 1 The synthesis of some secondary carbene complexes of d^6 metals by three-fragment oxidative addition: (*i*) *trans*-[Ru(CO)$_3$(PPh$_3$)$_2$]; (*ii*) PEt$_3$; (*iii*) *trans*-[IrCl(N$_2$)(PPh$_3$)$_2$]; (*iv*) *trans*-[Ir(CO)Cl(PPh$_3$)$_2$]; (*v*) Ag[PF$_6$]; (*vi*) *cis*-[Pt(η-C$_2$H$_4$)Cl$_2$(PEt$_3$)]; (*vii*) (a) [{Pt(η-C$_2$H$_4$)Cl$_2$}$_2$], (b) PEt$_3$
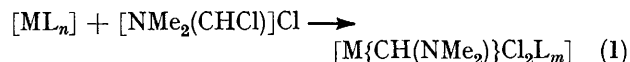
[(i)—(iii)] have emerged for the preparation of a wide variety of metal complexes having the ligand CH(NMe$_2$).

complex product has three of its ligands derived from the addendum.[2] In Part 7,[3a] such reactions were

$$[ML_n] + [NMe_2(CHCl)]Cl \longrightarrow [M\{CH(NMe_2)\}Cl_2L_m] \quad (1)$$

† No reprints available.

[1] Part 12, M. F. Lappert and P. L. Pye, *J.C.S. Dalton*, 1977, 2172.

[2] M. F. Lappert and A. J. Oliver, *J.C.S. Chem. Comm.*, 1972, 274.
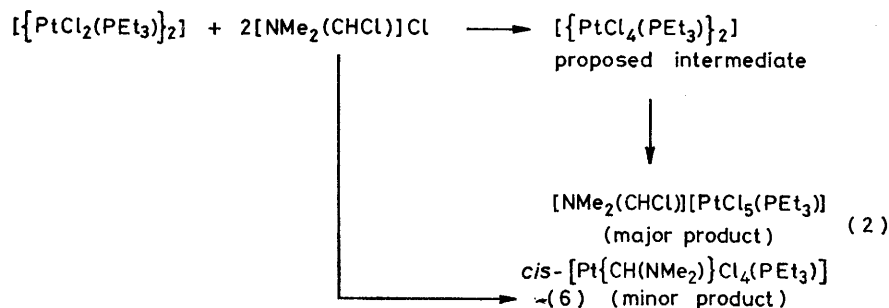
[3] (*a*) Part 7, B. Çetinkaya, M. F. Lappert, G. M. McLaughlin, and K. Turner, *J.C.S. Dalton*, 1974, 1591; (*b*) B. Çetinkaya, M. F. Lappert, and K. Turner, *J.C.S. Chem. Comm.*, 1972, 851.

reported for Rh^I $\longrightarrow$ Rh^{III} systems. [Below, we shall also refer to attempts to reduce the secondary carbene-rhodium(III) products.] We now describe extensions (Scheme 1) to other d^8 substrates: Ru^0, Ir^I, and Pt^{II}, the last of which was predicted in a preliminary communication.[3b]

The 18-electron complex [Ru(CO)$_3$(PPh$_3$)$_2$] afforded the adduct (1) with loss of two ligands rather than the one ligand lost by 16-electron substrates (e.g. a complex of Ir^I or Pt^{II}). Complex (1) was converted in high yield into the more soluble analogue [Ru{CH(NMe$_2$)}(CO)Cl$_2$-(PEt$_3$)$_2$] (2). Only one iridium(I) substrate, trans-[IrCl(N$_2$)(PPh$_3$)$_2$], was observed to give a three-fragment oxidative adduct; complex (3) was obtained with loss of the labile dinitrogen ligand. With the isoelectronic Vaska's compound, the ionic carbene complex [Ir-{CH(NMe$_2$)}(CO)Cl$_2$(PPh$_3$)$_2$]Cl (4) was formed. Presumably a rhodium analogue was not found in the corresponding rhodium series [the rhodium analogue of (3) was formed [3a]] because of the greater lability of CO in a rhodium(III) rather than an iridium(III) carbonyl-containing complex.

As shown in Scheme 1 the platinum substrates of choice for the synthesis of cis-[Pt{CH(NMe$_2$)}Cl$_4$(PEt$_3$)] (6)

shown in equation (2). The ionic (major) platinum(IV) product is believed to have formed via [Pt^{II}L$_n$] $\longrightarrow$ [Pt^{IV}Cl$_2$L$_n$] and bridge splitting by Cl$^-$. Support for this proposal is found in related oxidative additions. Thus, equation (1) is not invariably followed; exceptions include [Pt(PPh$_3$)$_3$] and trans-[Ir(CO)Cl(PMePh$_2$)$_2$], which gave cis-[PtCl$_2$(PPh$_3$)$_2$] and [Ir(CO)Cl$_3$(PMePh$_2$)$_2$], respectively. Similarly, [Pt(PPh$_3$)$_4$], with [NMe$_2$(CHCl)]-[BF$_4$], gave [{PtCl(PPh$_3$)$_2$}$_2$][BF$_4$]$_2$. There is some analogy with oxidative additions of alkyl halides RX to unsaturated substrates [ML$_n$]: possible products include [MR(X)L$_m$], [MX$_2$L$_m$], and [MH(X)L$_m$].[4]

Of the reactions of Scheme 1, that leading to the cationic iridium(III) complex does not strictly fall within

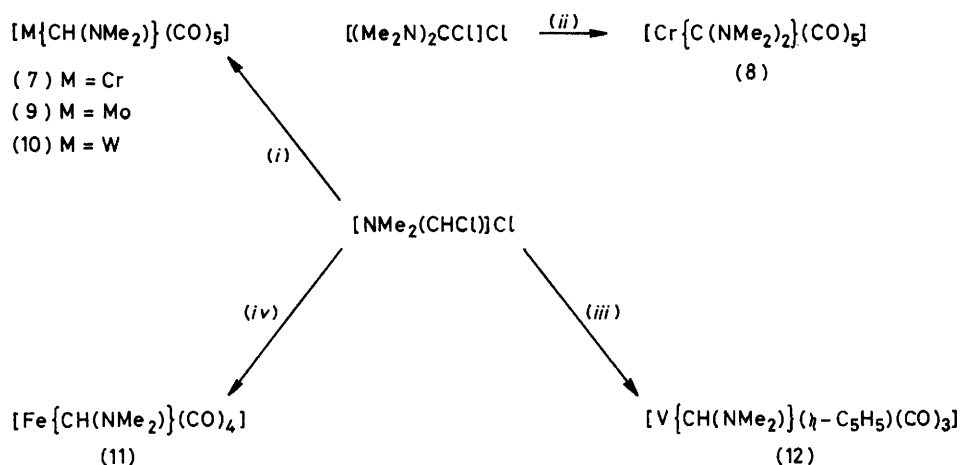$$[\{PtCl_2(PEt_3)\}_2] \;+\; 2[NMe_2(CHCl)]Cl \longrightarrow [\{PtCl_4(PEt_3)\}_2]$$

proposed intermediate

$$\downarrow$$

[NMe$_2$(CHCl)][PtCl$_5$(PEt$_3$)]
(major product)   (2)

cis-[Pt{CH(NMe$_2$)}Cl$_4$(PEt$_3$)]
(6) (minor product)

of the labile dinitrogen ligand. With the isoelectronic Vaska's compound, the ionic carbene complex [Ir-{CH(NMe$_2$)}(CO)Cl$_2$(PPh$_3$)$_2$]Cl (4) was formed. Presumably a rhodium analogue was not found in the corresponding rhodium series [the rhodium analogue of (3) was formed [3a]] because of the greater lability of CO in a rhodium(III) rather than an iridium(III) carbonyl-containing complex.

the scope of equation (1) because one of the three fragments constitutes the counter anion. Similar reactions have been described using as addendum a chelate methyleneammonium salt, e.g. the non-co-ordinating tetrafluoroborate as in [ClCN(Me)CH:C(Me)S][BF$_4$].[5]

$$Na_2[ML_m] + [NMe_2(CHCl)]Cl \longrightarrow$$
$$[M\{CH(NMe_2)\}L_m] + 2NaCl \quad (3)$$
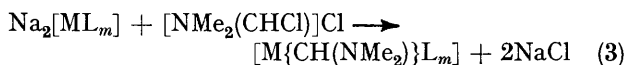
(ii) Salt Elimination.—Equation (3) illustrates this

[M{CH(NMe$_2$)}(CO)$_5$]   [(Me$_2$N)$_2$CCl]Cl $\xrightarrow{(ii)}$ [Cr{C(NMe$_2$)$_2$}(CO)$_5$]

(7) M = Cr
(9) M = Mo
(10) M = W

(i)

[NMe$_2$(CHCl)]Cl

(iv)   (iii)

[Fe{CH(NMe$_2$)}(CO)$_4$]   [V{CH(NMe$_2$)}(η-C$_5$H$_5$)(CO)$_3$]
(11)   (12)

(8)

SCHEME 2   The synthesis of some carbene complexes of d^4, d^6, and d^8 metals by salt elimination: (i) Na$_2$[M(CO)$_5$]; (ii) Na$_2$[Cr(CO)$_5$]; (iii) Na$_2$[V(η-C$_5$H$_5$)(CO)$_3$]; (iv) Na$_2$[Fe(CO)$_4$]

are [Pt(η-C$_2$H$_4$)Cl$_2$(PEt$_3$)] or [{Pt(η-C$_2$H$_4$)Cl$_2$}$_2$]. However, complex (6) was also obtained in poorer yields as

type of process. It has been realised for the five cases shown in Scheme 2. Of these, two were mentioned in a

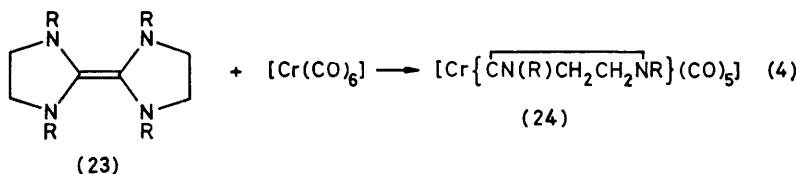[4] M. F. Lappert and P. W. Lednor, Adv. Organometallic Chem., 1976, 14, 345.

[5] P. J. Fraser, W. R. Roper, and F. G. A Stone, J.C.S. Dalton, 1974, 102.

preliminary communication,[3b] the carbene complexes of Cr^0 and Fe^0, (7) and (11). The formation of [Cr-{C(NMe$_2$)$_2$}(CO)$_5$] (8) is related to the general reaction of equation (3); another example was the conversion of PhC⋮C(Ph)CCl$_2$ into pentacarbonyl(2,3-diphenylcyclo-prop-2-enylidene)chromium(o).[6]

The complex [V{CH(NMe$_2$)}(η-C$_5$H$_5$)(CO)$_3$] (12) is

(21)   (22)
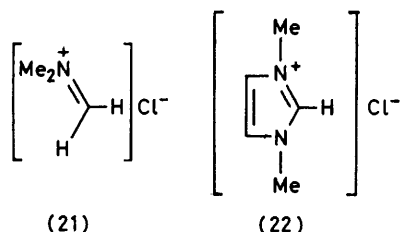
noteworthy, being a neutral Group 5 transition-metal derivative containing a nucleophilic carbene ligand.

obtained by the salt-elimination route, were modest. This is attributed mainly to the method used for the preparation of the Group 6 metal dianions. Thus, very little Na$_2$[M(CO)$_5$], particularly for M = Mo or W, is formed using sodium amalgam in refluxing tetrahydro-furan (thf).[8] The preparation of the vanadium complex (12) was accompanied by fairly extensive decomposition affording an amorphous black material; complex (12) is moderately air-sensitive in the solid state. The highest yield (8%) of [W{CH(NMe$_2$)}(CO)$_5$] was obtained using [NMe$_2$(CH$_2$)]Cl (21) as the carbene precursor rather than [NMe$_2$(CHCl)]Cl. Compound (21) was, shown to afford complexes (7) or (11) from respectively Na$_2$-[Cr(CO)$_5$] or Na$_2$[Fe(CO)$_4$].[9] Similarly, the salt (22) was a source of tertiary carbenemetal complexes, by reaction with Na[Cr(CO)$_5$H] or Na[Fe(CO)$_4$H].[10]

Apart from the five transition-metallate(2−) species employed in this work, Na$_2$[Ru(CO)$_4$] and Na$_2$[Os(CO)$_4$] have also been used as precursors to carbenemetal

(23)

This appears to be the first use of Na$_2$[V(η-C$_5$H$_5$)(CO)$_3$] in a salt-elimination reaction. The very interesting ylids of Nb^{III} and Ta^{III} obtained from a metal(v) chloride and a bulky alkyl-lithium are also known.[7a] Niobium(v)

complexes.[11] The reduction of [M(η-C$_5$H$_5$)(CO)$_4$] (M = Nb or Ta) has not yet been reported; by analogy with the vanadium complex (12), the derived dianions should provide a route to carbene-niobium and -tantalum
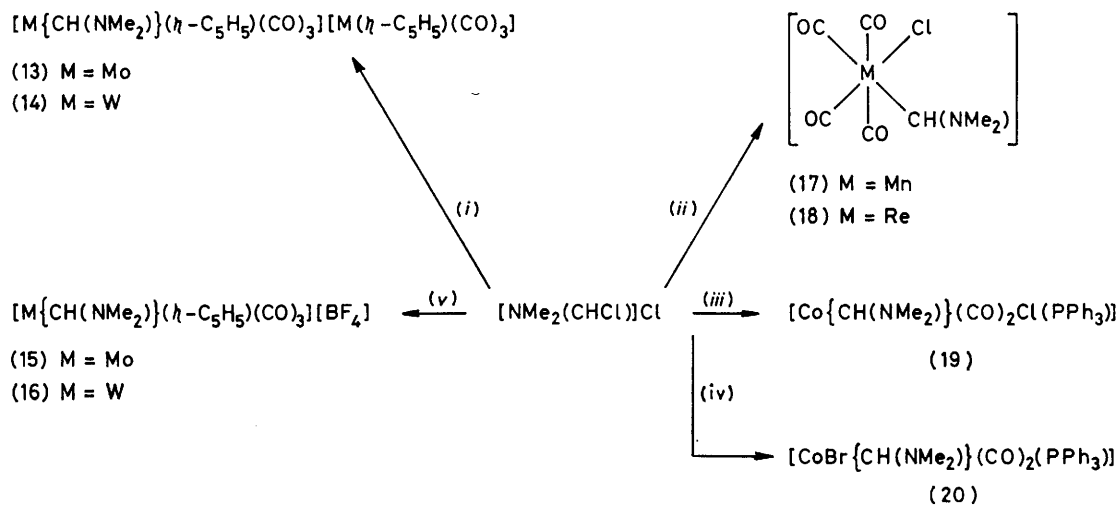
Scheme 3   The synthesis of some secondary carbene complexes of d^6 and d^8 metals by salt elimination with concomitant oxidative-addition: (i) 2 Na[M(η-C$_5$H$_5$)(CO)$_3$]; (ii) Na[M(CO)$_5$]; (iii) Na[Co(CO)$_3$(PPh$_3$)]; (iv) [NMe$_2$(CHBr)]Br; (v) (a) Na[M(η-C$_5$H$_5$)(CO)$_3$], (b) Na[BF$_4$]

or tantalum(v) chloride with successively MeNC and H$^+$ gave complexes formulated as containing [M{CCl-(NHMe)}Cl$_4$]$^+$.[7b]

The yields of the carbenemetal complexes (7)—(12),

derivatives. By comparison with the series [V(η-C$_5$H$_5$)(CO)$_4$], [Cr(CO)$_6$], and [Fe(CO)$_5$], which yield corresponding dianions with loss of CO, [Mn(η-C$_5$H$_5$)-(CO)$_3$] might also have been expected to provide a

[6] K. Öfele, Angew. Chem. Internat. Edn., 1969, 8, 916.

[7] (a) R. R. Schrock, J. Amer. Chem. Soc., 1974, 96, 6796; (b) B. Crociani and R. L. Richards, J.C.S. Chem. Comm., 1973, 127.

[8] B. D. Dombek and R. J. Angelici, J. Amer. Chem. Soc., 1973, 95, 7516.

[9] C. W. Fong and G. Wilkinson, J.C.S. Dalton, 1975, 1100.

[10] K. Öfele and M. Herberhold, Angew. Chem. Internat. Edn., 1970, 9, 739.

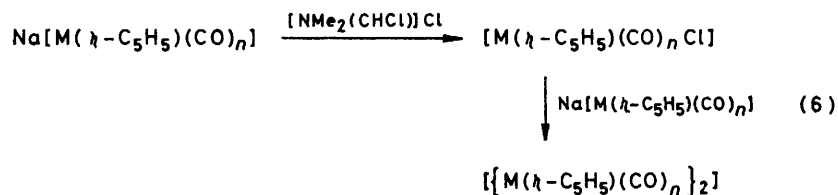[11] M. Green, F. G. A. Stone, and M. Underhill, J.C.S. Dalton, 1975, 939.

dianion; surprisingly, on reduction only $[Mn(CO)_5]^-$ was observed.[12] The number of mononuclear metallate(2—) complexes is clearly small, and this is a limitation of the salt-elimination route to carbenemetal complexes.

The complex $[Cr\{C(NMe_2)_2\}(CO)_5]$ (8) and an iron analogue $[Fe\{C(NMe_2)_2\}(CO)_4]$ [13] are of interest as potential models for study of electron-rich olefin dismutation (*cf.* ref. 14) because tetrakis(dimethylamino)ethylene (tdae), unlike chelate analogues (23), is *not* a source of corresponding carbene complexes [*e.g.* equation (4) (R = Me, Et, or $PhCH_2$)].[15] We now find that complexes (8) and (24) are very similar in thermal stability and spectroscopic properties, suggesting that product stability or bond strengths are not factors in the failure of tdae to afford carbenemetal complexes.

(iii) Salt Elimination with Concomitant Oxidative Addition.—The general equation (5) defines this process. It is illustrated in Scheme 3 for nine secondary carbenemetal complexes, three of which [(13), (14), and (19)]

$$Na[ML_m] + [NMe_2(CHCl)]Cl \longrightarrow$$
$$[M\{CH(NMe_2)\}ClL_n] + NaCl \quad (5)$$
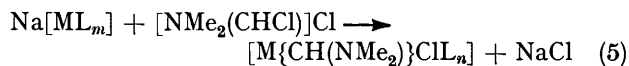
were mentioned in a preliminary communication.[16] A related reaction, that between $Na[Mn(CO)_5]$ and for example $[ClCN(Me)CH\!:\!C(Me)S][BF_4]$, has been described.[17] The transition-metal substrates fall into two

the more nucleophilic monoanions. Even the least nucleophilic metallate mentioned in ref. 19, $[Co(CO)_4]^-$, reacts (as the sodium salt) with $[NMe_2(CHCl)]Cl$ to afford the cluster compound (25).[20] It is interesting

(25)
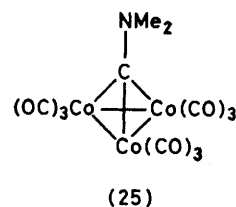
(Scheme 3) that phosphine substitution prevents cluster formation. Complexes (19) and (20) are rare examples of carbene complexes of cobalt.

Characterisation of New Complexes.—All the carbenemetal complexes were identified on the basis of their elemental analyses, and i.r. and n.m.r. spectra [Tables (1)—(3)].

The stereochemistry of $[Ru\{CH(NMe_2)\}(CO)Cl_2(PEt_3)_2]$ (2) was deduced from the following spectroscopic data. The ^{31}P n.m.r. spectrum consisted of a singlet indicating equivalent phosphines, while in the ^1H n.m.r. spectrum the CH_3 groups of the PEt_3 ligands appeared as a quintet showing that the phosphines are mutually *trans*. The proton-decoupled ^{13}C n.m.r. spectrum contained two triplets [δ 248.5 p.p.m.(^2J 11.0 Hz)

classes, those without labile carbonyl groups which give cationic complexes [(13)—(16)] and those with easily replaced carbonyl groups which give neutral complexes [(17)—(20)].

The reaction class of equation (5) has not been found to be of general application. Thus, carbene complexes were not isolated (instead the dimers $[\{M(\eta\text{-}C_5H_5)(CO)_n\}_2]$ using $[Fe(\eta\text{-}C_5H_5)(CO)_2]^-$ or $[Ni(\eta\text{-}C_5H_5)(CO)]^-$, although carbene complexes have been prepared from these anions using reagents other than $[NMe_2(CHCl)]Cl$.[18] A possible reaction sequence is shown in equation (6). The first step, *i.e.* oxidation without carbene incorporation, has precedent [see above under (*i*)]. It is interesting to note that carbene incorporation does not occur for

and δ 203.0 p.p.m. (^2J 14.4 Hz)] assigned to the carbene and CO ligands, respectively. The magnitude of the ^{13}C-^{31}P coupling constants is consistent [21] with the carbene and CO ligands being *cis* to the phosphines. The i.r. spectrum contained bands at 296w and 245m cm^{-1} due to mutually *cis* Ru–Cl bonds. A similar stereochemistry has been proposed for another secondary carbeneruthenium(II) complex.[22]

The assignment of the configuration of *cis*-$[Pt\{CH(NMe_2)\}Cl_4(PEt_3)]$ (6) is based on i.r. ($PtCl_4$ stretching modes) and ^1H n.m.r. (the lack of ^{31}P coupling to $C_{carb.}$–H) data. Furthermore, the position of $\nu(C_{carb.}$–N) is appropriate for a carbene *trans* to a chloride ligand.[3a]

The complex $[Ir\{CH(NMe_2)\}Cl_3(PPh_3)_2]$ (3) is assumed

[12] J. E. Ellis, R. A. Faltynek, and S. G. Hentges, *J. Organometallic Chem.*, 1976, **120**, 389.

[13] W. Petz, *Angew. Chem. Internat. Edn.*, 1975, **14**, 367.

[14] D. J. Cardin, M. J. Doyle, and M. F. Lappert, *J.C.S. Chem. Comm.*, 1972, 927.

[15] Part 11, P. B. Hitchcock, M. F. Lappert, and P. L. Pye, *J.C.S. Dalton*, 1977, 2160.

[16] A. J. Hartshorn, M. F. Lappert, and K. Turner, *J.C.S. Chem. Comm.*, 1975, 929.

[17] P. J. Fraser, W. R. Roper, and F. G. A. Stone, *J.C.S. Dalton*, 1974, 760.

[18] D. J. Cardin, B. Çetinkaya, and M. F. Lappert, *Chem. Rev.*, 1972, **72**, 545.

[19] R. E. Dessy, R. L. Pohl, and R. B. King, *J. Amer. Chem. Soc.*, 1966, **88**, 5121.

[20] D. Seyferth, J. E. Hallgren, and P. L. K. Hung, *J. Organometallic Chem.*, 1973, **50**, 265.

[21] P. B. Hitchcock, M. F. Lappert, and P. L. Pye, *J.C.S. Chem. Comm.*, 1977, 196; M. F. Lappert and P. L. Pye, Part 16, to be published.

[22] D. F. Christian and W. R. Roper, *J. Organometallic Chem.*, 1974, **80**, C35.

TABLE 1

Characterisation data for new secondary carbenemetal complexes and $[Cr\{C(NMe_2)_2\}(CO)_5]$

	Complex	Colour	M.p. ($\theta_c/°C$)	Yield (%)	C	H	N	Cl
					* Analysis (%)			
(1)	$[Ru\{CH(NMe_2)\}(CO)Cl_2(PPh_3)_2]$	White	250	75	61.8(61.5)	4.8(5.2)	1.9(1.8)	9.5(9.1)
(2)	$[Ru\{CH(NMe_2)\}(CO)Cl_2(PEt_3)_3]$	White	166	91	39.1(39.0)	7.6(7.7)	2.9(2.8)	14.7(14.4)
(3)	$[Ir\{CH(NMe_2)\}Cl_3(PPh_3)_2]$	White	274—276	69	53.4(53.2)	4.2(4.2)	1.6(1.6)	
(4)	$[Ir\{CH(NMe_2)\}(CO)Cl_2(PPh_3)_2]Cl·CHCl_3$	White	176—185	79	47.7(47.9)	3.7(3.7)	1.4(1.4)	
(5)	$[Ir\{CH(NMe_2)\}(CO)Cl_2(PPh_3)_2][PF_6]$	White	245—248	95	47.1(47.0)	3.7(3.7)	1.4(1.4)	
(6)	$[Pt\{CH(NMe_2)\}Cl_4(PEt_3)]$	Yellow	138—140	86	21.7(21.2)	4.3(4.3)	2.8(2.7)	
(7)	$[Cr\{CH(NMe_2)\}(CO)_5]$	Yellow	64—66	40	38.6(38.6)	2.8(2.8)	5.3(5.6)	
(8)	$[Cr\{C(NMe_2)_2\}(CO)_5]$	Yellow	102	24	41.0(41.1)	4.2(4.1)	9.4(9.5)	
(9)	$[Mo\{CH(NMe_2)\}(CO)_5]$	Fawn	56—58	18	32.6(32.8)	2.6(2.4)	4.7(4.8)	
(10)	$[W\{CH(NMe_2)\}(CO)_5]$	Yellow	75—76	8	24.8(25.2)	2.1(1.9)	3.7(3.7)	
(11)	$[Fe\{CH(NMe_2)\}(CO)_4]$	Yellow	55—56	52	37.0(37.4)	3.3(3.1)	6.3(6.2)	
(12)	$[V\{CH(NMe_2)\}(\eta\text{-}C_5H_5)(CO)_3]$	Yellow	120	20	50.9(51.3)	5.0(4.7)	5.3(5.4)	
(13)	$[Mo\{CH(NMe_2)\}(\eta\text{-}C_5H_5)(CO)_3][Mo(\eta\text{-}C_5H_5)(CO)_3]$	Yellow	140 (decomp.)	81	41.6(41.7)	3.1(3.1)	2.5(2.6)	
(14)	$[W\{CH(NMe_2)\}(\eta\text{-}C_5H_5)(CO)_3][W(\eta\text{-}C_5H_5)(CO)_3]$	Yellow	127—128 (decomp.)	87	31.6(31.6)	2.5(2.4)	1.8(1.9)	
(15)	$[Mo\{CH(NMe_2)\}(\eta\text{-}C_5H_5)(CO)_3][BF_4]$	Yellow	150	65	34.2(34.0)	3.2(3.1)	3.7(3.6)	
(16)	$[W\{CH(NMe_2)\}(\eta\text{-}C_5H_5)(CO)_3][BF_4]$	Yellow	156—157	62	27.8(27.7)	2.5(2.5)	2.9(2.9)	
(17)	$[Mn\{CH(NMe_2)\}(CO)_4Cl]$	Yellow	91—93	22	32.4(32.4)	2.7(2.7)	5.5(5.4)	
(18)	$[Re\{CH(NMe_2)\}(CO)_4Cl]$	Fawn	96—98	58	21.5(21.5)	1.7(1.8)	3.0(2.7)	9.0(9.1)
(19)	$[Co\{CH(NMe_2)\}(CO)_2Cl(PPh_3)]$	Yellow	178—180	45	58.8(58.8)	5.0(5.7)	3.0(3.0)	7.6(7.5)
(20)	$[CoBr\{CH(NMe_2)\}(CO)_2(PPh_3)]$	Yellow	185	72	53.5(53.7)	4.3(4.3)	2.5(2.7)	
(30)	$[Rh\{CH(NMe_2)\}Cl_2H(PPh_3)_2]$	Yellow	238—240 (decomp.)	40	61.7(61.9)	5.1(5.1)	2.0(1.8)	
(31)	$[Rh\{CH(NMe_2)\}Cl_2H(PEt_3)_2]$	Yellow-orange	112—118 (decomp.)	69	37.9(38.5)	8.5(8.2)	2.9(3.0)	
(32)	$[Rh\{CH(NMe_2)\}Cl_2H(PMe_2Ph)_2]$	Yellow	210—212	92	44.7(44.9)	5.3(5.9)	2.1(2.8)	

* Calculated values are given in parentheses.

TABLE 2

Infrared and ¹H n.m.r. spectroscopic data for the new complexes

	I.r. (cm⁻¹)				¹H N.m.r.(τ)				
	ν(C–N) a	ν(M–Cl) a	ν(C–O) [or ν(RhH)]	ν(anion)	Solvent	$C_{carb.}$–H	N–CH₃ (cis)	N–CH₃ (trans)	Other
(1)	1 571	298w, 252m	1 962 a		(D₃C)₂SO	−0.90	7.22(s)	7.77(s)	P–C₆H₅, 3.3(m)
(2)	1 553	296w, 254m	1 922 a		CDCl₃	−0.53	6.20(s)	6.27(s)	P–CH₂CH₃, 7.82(m); P–CH₂CH₃, 8.60(m)
(3)	1 584	329m, 310w, 280w			(D₃C)₂SO	b	6.55(s)	6.68(s)	P–C₆H₅, 2.4(m)
(4)	1 612	321w, 291m	2 073s a		CDCl₃	0.53(br,s)	6.59(s)	6.92(s)	P–C₆H₅, 1.86(m), 2.44(m)
(5)	1 608	317w, 292m	2 080s a	ν(PF₆) 840s,br a	CD₂Cl₂	0.28(br,s)	7.00(s)	7.28(s)	P–C₆H₅, 1.90(m), 2.44(m)
(6)	1 632	346m, 332m, 285s			CDCl₃	1.07(s)	6.72(s)	7.00(s)	P–CH₂CH₃, 8.17(m); P–CH₂CH₃, 9.20(m)
(7)	1 545		2 059w, 1 930s c		CDCl₃, C₆D₆	−0.86(s), −0.15(s)	6.25(d), *J 0.9 Hz 7.20(s)	6.43(d), *J 1.3 Hz 7.97(s)	
(8)	1 491		2 052w, 1 983w, 1 930s c		CDCl₃, C₆D₆				N(CH₃)₂, 6.78(s); N(CH₃)₂, 7.53(s)
(9)	1 540		2 068w, 1 939s c		CDCl₃	−0.80(s)	6.34(s)	6.47	
(10)	1 550		2 068w, 1 990w, 1 930s e		CDCl₃, C₆D₆	−0.95(s), −0.15(s)	6.40(d), *J 0.7 Hz 7.43(s)	6.48(d), *J 1.2 Hz 8.08(s)	
(11)	1 557		2 049m, 1,976m c 1 947s, 1 933s		CDCl₃	−1.10(s)	6.37(s)	6.50(s)	
(12)	1 531		1 956m, 1 881m, 1 863s c		C₆D₆	−0.20(s)	7.23(s)	7.65(s)	C₅H₅ 5.13(s)
(13)	1 588		2 057m, 1 973s, 1 889m, 1 773s, 1 753s d		(D₃C)₂SO	−1.00(s)	6.39(s)	6.48(s)	C₅H₅: cation 3.92(s); anion 5.02(s)
(14)	1 585		2 053m, 1 975s, 1 959s 1 885m, 1 773s, 1 749s d		(D₃C)₂SO	−1.00(s)	6.32(s)	6.48(s)	C₅H₅; cation 3.78(s); anion 4.97(s)
(15)	1 601		2 045m, 1 975s, 1 905s d	ν(BF₄) 1 060s,br a	(D₃C)₂SO	−0.95(s)	6.20(s)	6.51(s)	C₅H₅, 3.95(s)
(16)	1 601		2 065m, 1 945s, 1 878s d	ν(BF₄) 1 060s,br a	(D₃C)₂SO	−1.02(s)	6.28(s)	6.47(s)	C₅H₅, 3.76(s)
(17)	1 596	262	2 091w, 2 027m, 2 013s, 1 945m e		CDCl₃	−0.95(s)	6.22(s)	6.30(s)	
(18)	1 602	265	2 095w, 2 051m, 2 006s, 1 931m e		CDCl₃	−0.83(s)	6.27(d), *J 0.9 Hz	6.35(d), *J 1.3 Hz	
(19)	1 582	245	1 991m, 1 925s d		(D₃C)₂CO	−0.95(s)	6.20(s)	6.23(s)	P–C₆H₅, 2.5(m)
(20)	1 590		1 998m, 1 925s d		(D₃C)₂CO	−0.90(s)	6.23(s)	6.28(s)	P–C₆H₅, 2.5(m)
(30)	1 586	296w	[ν(Rh–H), 2 170m] a		(insoluble)				
(31)	1 570	336w	[ν(Rh-H), 2 128ms] a		CDCl₃	−1.23(br)	6.38(s)	6.44(s)	P–CH₂CH₃, 8.15(m), 9.90(qn); Rh–H, 26.81(d) [¹J(Rh–H) 26.5; ¹J(P–H) 13.2 Hz]
(32)	1 602	319w	[ν(Rh–H), 2 110m] a		CDCl₃	0.74(br)	7.34(s)	7.62(s)	P–CH₃, 8.26(t)

a Paraffin mull.   b Not observed.   c In hexane.   d In dichloromethane.   e In chloroform.

to have a *mer* configuration of the chloride ligands and *trans* phosphines, like the most stable form of the rhodium analogue.[3a] Other isomers of the latter have been prepared; for example, if benzene was used as the reaction solvent, a complex with a *mer* arrangement of chloride ligands and *cis* phosphines was obtained, but isomerisation occurred in chlorinated solvents, with ν(C–N) for the carbene ligand sensitive to this change in stereochemistry.

The cation $[Ir\{CH(NMe_2)\}(CO)Cl_2(PPh_3)_2]^+$ (4) derived from (5) is isostructural with the ruthenium(II) complexes (1) or (2) and has the same stereochemistry. The [31]P n.m.r. spectrum showed a singlet, whilst the [13]C n.m.r.

The i.r. spectra are also a useful diagnostic tool of carbenemetal complex formation.[3a] A strong absorption assigned to ν(C ⋯ N) was observed in the range 1 535—1 640 cm^{-1}. Generally, absorptions at the higher end of the range are due to carbene co-ordinated to metals in a higher oxidation state, without strong σ-donor ligands, and *vice versa*.

Reduction of some Secondary Carbenerhodium(III) Complexes.—The results are summarised in Scheme 4. It had been hoped to convert secondary carbenerhodium(III) complexes [3] into rhodium(I) derivatives without Rh–$C_{carb.}$ bond cleavage. This type of reaction would certainly have been useful, because none of the general

Complex	Solvent	$C_{carb.}$	N-CH$_3$(*cis*)	N-CH$_3$(*trans*)	CO, and other
(2)	CDCl$_3$	248.5 [a]	54.2	45.3	203.0 [b]
(4)	(D$_3$C)$_2$SO	192.7 [c]	54.0	46.5	158.8 [c]
(7)	CDCl$_3$	264.2	55.4	46.5	224.0,[d] 217.5 [e]
(15)	(D$_3$C)$_2$SO	231.4	55.0	47.2	231.4,[d] 225.0,[f] C$_5$H$_5$ 96.3
(16)	(D$_3$C)$_2$SO	215.5 [g]	54.5	47.5	220.4,[d,h] 214.8,[f,i] C$_5$H$_5$ 95.1
(17)	CDCl$_3$	256.8	56.8	47.6	218.3,[d] 212.9,[d] 210.4 [f]

[a] [2]J([31]P–[13]C) 22.0 Hz. [b] [2]J([31]P–[13]C) 26.9 Hz. [c] [2]J([31]P–[13]C) 3 Hz. [d] One CO. [e] Four CO. [f] Two CO. [g] [1]J([183]W–[13]C) 70.0 Hz. [h] [1]J([183]W–[13]C) 125.1 Hz, one CO. [i] [1]J([183]W–[13]C) 138.2 Hz, two CO.

spectroscopic data for $C_{carb.}$ and CO showed two poorly resolved triplets with surprisingly small coupling constants of $^2J(^{31}P–^{13}C_{carb.})$ 3 Hz and $^2J(^{31}P–^{13}CO) \approx 3$ Hz. The high-field position (*ca.* 160 p.p.m.) of the carbonyl carbon has been observed for other iridium(III) species.[23]

Other Spectroscopic Data.—Secondary carbenemetal complexes have i.r. and n.m.r. features very similar to dialkylformamides and $[NMe_2(CHCl)]Cl$.[3a]

The most useful diagnostic tool is undoubtedly the [13]C n.m.r. spectrum. Chemical shifts of $C_{carb.}$ are in the range *ca.* 195—250 p.p.m. downfield from SiMe$_4$, while the carbon in $[NMe_2(CHCl)]Cl$ is at 164 p.p.m. In complexes where their chemical shifts are similar, the secondary carbene carbon can easily be distinguished from co-ordinated CO by its greater intensity, the relaxation time of which is significantly shorter than that of CO. Uncertainties are resolved by the ^{1}H undecoupled ^{13}C spectrum, which exhibits either a doublet or a considerably broadened $C_{carb.}$ resonance.

The [1]H n.m.r. spectra exhibit $C_{carb.}$–H resonances in the range τ −1.5 to +1 compared with $[NMe_2(CHCl)]Cl$ at τ −1.1, and two CH$_3$ resonances from the magnetically non-equivalent N-alkyl groups at higher field. The chemical shifts and shift differences of the N-alkyl groups are strongly solvent dependent (see Table 2). In some cases, *e.g.* complexes (7) or (18), coupling between $C_{carb.}$–H and the N–CH$_3$ groups is observed (see also ref. 3); the magnitude of the coupling constant can be used to identify the methyl groups *cis* or *trans* to the secondary carbene ligand. The *cis* methyl is observed at lower field than the *trans*.

methods (*i*)—(*iii*) provide access to such complexes. The experiments were based on the analogy with Rh[III] ⟶ Rh[I] conversions [24] of phosphinerhodium complexes. However, the only new carbene complexes are some interesting hydrido(secondary carbene)rhodium(III) derivatives (30)—(32).

The assignments of stereochemistry shown in Scheme 4 are based on the spectroscopic data given in the Experimental section, and in part by analogy with such data obtained for complex (33), which has been characterised by X-ray crystallography.[3a] The values of ν(Rh–H) for the three carbenehydridorhodium(III) complexes $[Rh\{CH(NMe_2)\}Cl_2H(PR_3)_2]$ (30)—(32) decrease in the sequence $PR_3 = PPh_3 > PEt_3 > PMe_2Ph$. A similar comparison on the basis of the chemical shift of Rh–*H* was not possible because only complex (31) was adequately soluble. The $C_{carb.}$–*H* resonance of $[Rh\{CH(NMe_2)\}Cl_2H(PEt_3)_2]$ (31) was at τ −1.23, but showed no clearly resolved splitting from ^{31}P and [103]Rh nuclei, although such splitting was observed [3] for (27) and also for complex (31) for the Rh–*H* resonance (a 1 : 2 : 2 : 2 : 1 quintet from two sets of overlapping triplets). The carbenehydridometal complexes were previously limited to a single example, a cationic platinum(II) complex.[25]

The i.r. spectrum of $[Rh\{CH(NMe_2)\}Cl_2H(PPh_3)_2]$ (30) has ν(Rh–H) at 2 170 cm^{-1} and a high ν(CN) at 1 586 cm^{-1}, indicating that the H[-] and CH(NMe$_2$) ligands are not mutually *trans*, while the weak ν(RhCl) at 296 cm^{-1} suggests that the two Cl^{-} ligands are not mutually *trans*. This leaves two possible configurations: that shown in (30), or its isomer in which Cl^{-} and PPh$_3$ are interchanged. The former is preferred because of

[23] M. F. Lappert and P. L. Pye, unpublished work.
[24] A. Sacco, R. Ugo, and A. Moles, *J. Chem. Soc. (A)*, 1966, 1670; J. Chatt and B. L. Shaw, *ibid.*, p. 1437.

[25] Part 8, B. Çetinkaya, P. Dixneuf, and M. F. Lappert, *J.C.S. Dalton*, 1974, 1827.

its synthesis in quantitative yield from the structurally authenticated [3a] $[\text{Rh}\{\text{CH(NMe}_2)\}\text{Cl}_3(\text{PPh}_3)_2]$ (34), and on the basis of relative *trans* influences. Complexes (31) and (32) have the same configuration as (30), from ^{31}P and ^{1}H n.m.r. spectra and i.r. characteristics. The position of ν(Rh–H) for complexes (30)—(32) may be

(30), and thus obtain a secondary carbenerhodium(I) product. Aniline gave no reaction, but NMe_3 gave a product having no Rh–H bond (i.r. evidence); purification was attempted by multiple crystallisations from dichloromethane, which gave $[\text{Rh}\{\text{CH(NMe}_2)\}\text{Cl}_3\text{-}(\text{PPh}_3)_2]$. Reaction of (26) with the strongly reducing [27]
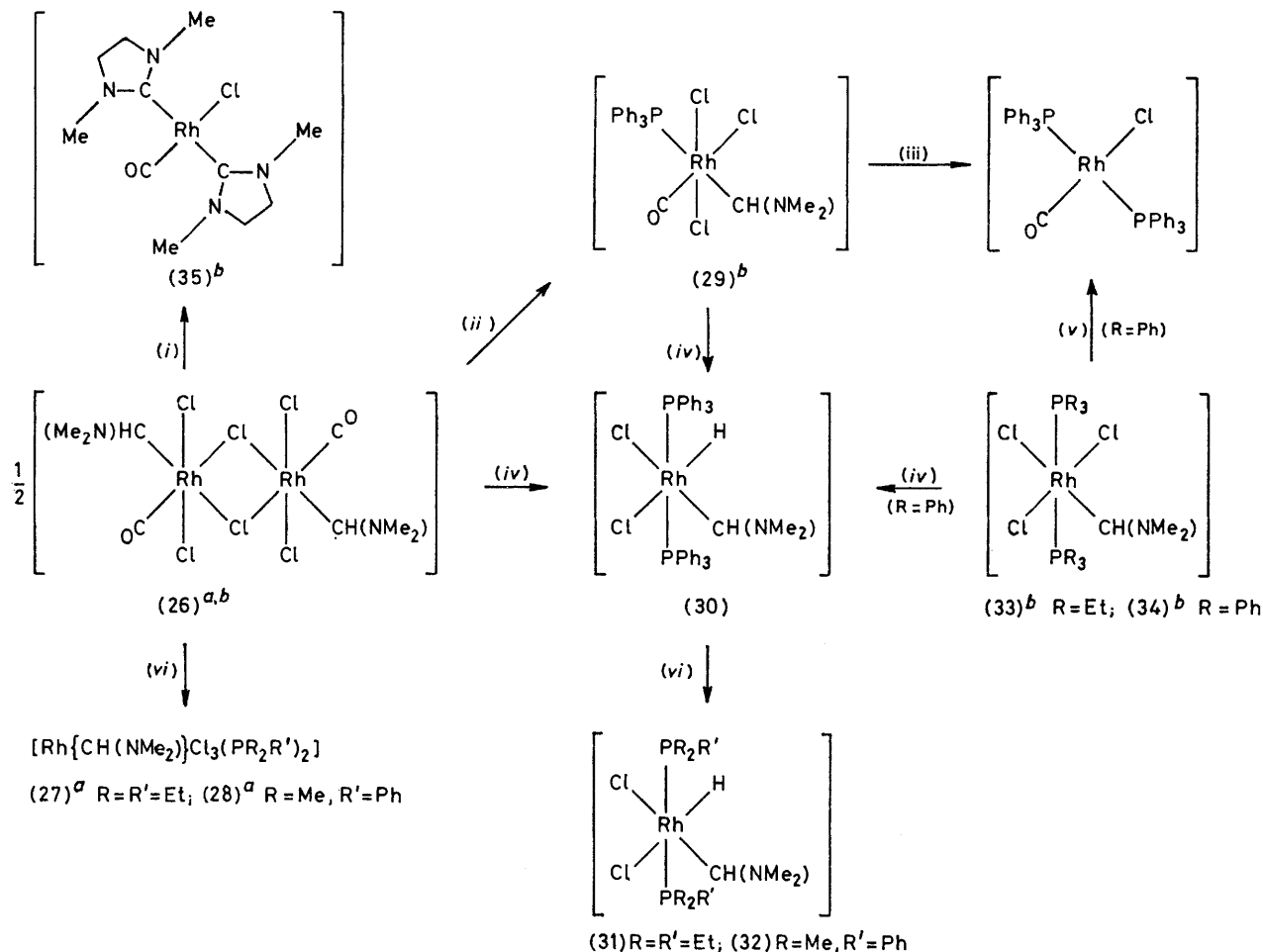
SCHEME 4   Attempted reductions of some secondary carbenerhodium(III) complexes

a Complexes (27) and (28) do not react with PPh_3–EtOH under conditions similar to those used for (26), (29), (33), and (34). *b* Complexes (26)—(29), (33), and (34) were reported elsewhere (ref. 3a); (35) is in refs. 25 and 38. (i) $(\overline{\text{NMeCH}_2\text{CH}_2\text{NMeC}})_2$; (ii) PPh_3 (1 mol); (iii) excess of PPh_3; (iv) PPh_3, EtOH; (v) K[OH], EtOH; (vi) $\text{PR}_2\text{R}'$.

compared with that for $[\text{RhCl}_2\text{H(PR}_3)_3]$ which have a meridional arrangement of PR_3 ligands; those with *trans*-H,Cl or *trans*-H,PR_3 arrangements, named α and β respectively,[26] where ν(Rh–H) is lower for the β isomers. This provides further support for structure (30) (rather than the β isomer), assuming that carbene and phosphine have similar *trans* influences.

Attempts were made to dehydrochlorinate complex

electron-rich olefin (23; R = Me) afforded complex (35) by carbene exchange.

EXPERIMENTAL

General procedures have been described in previous publications.[1,3a] The salt $[\text{NMe}_2(\text{CHCl})]\text{Cl}$ was prepared by the addition of COCl_2 to dimethylformamide in toluene.[28] Other starting materials were prepared by standard literature methods: $[\text{Ru(CO)}_3(\text{PPh}_3)_2]$,[29] $[\text{IrCl(N}_2)(\text{PPh}_3)_2]$,[30] $[\text{Ir(CO)Cl(PPh}_3)_2]$,[31] $[\text{Pt}(\eta\text{-C}_2\text{H}_4)\text{Cl}_2(\text{PEt}_3)]$,[32] $[\{\text{Pt}(\eta\text{-C}_2\text{H}_4)\text{-}$

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[31] R. A. Schunn and W. G. Peet, *Inorg. Synth.*, 1972, **13**, 128.

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$Cl_2\}_2]$,[33] $[V(\eta\text{-}C_5H_5)(CO)_4]$,[34] $[\{Mo(\eta\text{-}C_5H_5)(CO)_3\}_2]$,[34] $[\{Co\text{-}(CO)_3(PPh_3)\}_2]$,[35] $[\{Rh[CH(NMe_2)](CO)Cl_3\}_2]$,[3a] and $[Rh\text{-}\{CH(NMe_2)\}Cl_3(PEt_3)_2]$.[3a]

Carbonyldichloro(dimethylaminomethylene)bis(triphenylphosphine)ruthenium(II) (1).—To a solution or suspension of $[Ru(CO)_3(PPh_3)_2]$ (2.33 g, 4.5 mmol) in thf (50 cm³) was added $[NMe_2(CHCl)]Cl$ (0.57 g, 4.5 mmol) in portions at room temperature. After 1 h the mixture was heated under reflux for 15 min and then cooled and filtered to afford the white *product* (1.99 g).

Carbonyldichloro(dimethylaminomethylene)bis(triethylphosphine)ruthenium(II) (2).—To a suspension of (1) (1.18 g, 2 mmol) in benzene (30 cm³) was added triethylphosphine (0.65 cm³, 6 mmol). The solution was boiled under reflux until it became clear (*ca.* 4 h). Hexane (40 cm³) was added to the hot solution and the solution was allowed to cool to room temperature. Colourless crystals formed. Crystallisation was completed overnight at −20 °C to afford the *product* (0.897 g).

Trichloro(dimethylaminomethylene)bis(triphenylphosphine)iridium(III) (3).—To a solution of $[IrCl(N_2)(PPh_3)_2]$ (0.390 g, 0.5 mmol) in chloroform at 0 °C was added $[NMe_2(CHCl)]Cl$ (0.064 g, 0.5 mmol). The solution was stirred for 0.5 h while allowing it to warm to room temperature. A white *powder* was isolated (0.303 g).

Carbonyldichloro(dimethylaminomethylene)bis(triphenylphosphine)iridium(III) *Chloride–Chloroform* (1/1)(4).—To a solution of $[Ir(CO)Cl(PPh_3)_2]$ (0.525 g, 0.672 mmol) in chloroform (20 cm³) was added $[NMe_2(CHCl)]Cl$ (0.086 g, 0.672 mmol). After stirring for 0.5 h a colourless solution was obtained. Addition of hexane and cooling to −30 °C afforded a white *powder* (0.482 g).

Carbonyldichloro(dimethylaminomethylene)bis(triphenylphosphine)iridium(III) *Hexafluorophosphate* (5).—To a solution of $[Ir\{CH(NMe_2)\}(CO)Cl_2(PPh_3)_2]Cl$ (0.238 g, 0.232 mmol) in dichloromethane (10 cm³) was added silver(I) hexafluorophosphate (0.075 g, 0.297 mmol). After stirring for 2 h the solution was cloudy. Filtration gave a colourless solution which was reduced in volume and after addition of hexane afforded white *needles* (0.224 g).

Tetrachloro(dimethylaminomethylene)(triethylphosphine)-platinum(IV) (6).—To a solution of $[Pt(\eta\text{-}C_2H_4)Cl_2(PEt_3)]$ (0.243 g, 0.594 mmol) in chloroform was added $[NMe_2(CHCl)]Cl$ (0.076 g, 0.594 mmol). After 1 h a yellow solution was obtained which, on addition of diethyl ether, gave a yellow oily solid. Trituration with diethyl ether gave a yellow *solid* (0.261 g).

Pentacarbonyl(dimethylaminomethylene)chromium(0) (7).—Hexacarbonylchromium (2.20 g, 10 mmol) was added to a mixture of sodium amalgam (5 cm³, 1%) and thf (40 cm³). The solution was stirred vigorously and heated under reflux for 14 h. The solution was cooled, filtered, and $[NMe_2(CHCl)]Cl$ (1.32 g, 10.3 mmol) was added in portions over a period of 0.5 h. The solution was then stirred for 3 h, evaporated to dryness, and the residue extracted with boiling hexane (2 × 20 cm³). Cooling to −30 °C afforded yellow *needles* (0.996 g).

[Bis(dimethylamino)methylene]pentacarbonylchromium(0) (8).—This complex was prepared in a similar manner to (7); use of $[Cr(CO)_6]$ (1.10 g, 5 mmol) and $[(Me_2N)_2CCl]Cl$ (0.423 g, 3 mmol) afforded yellow *needles* (0.350 g).

Pentacarbonyl(dimethylaminomethylene)molybdenum(0) (9).—To $[Mo(CO)_6]$ (2.64 g, 10 mmol) was added a mixture of sodium amalgam (5 cm³, 1%) and thf (40 cm³). The solution was stirred at room temperature until CO evolution had ceased (*ca.* 4 h). The solution was then heated under reflux for 5 h, cooled, and filtered. The complex was then prepared in a similar manner to (7) and afforded fawn *needles* (0.525 g).

Pentacarbonyl(dimethylaminomethylene)tungsten(0) (10).—This complex was prepared in a similar manner to (7); use of $[W(CO)_6]$ (1.74 g, 5 mmol) and $[NMe_2(CHCl)]Cl$ (0.468 g, 5 mmol) afforded yellow *needles* (0.152 g).

Tetracarbonyl(dimethylaminomethylene)iron(0) (11).—The salt $Na_2[Fe(CO)_4]\cdot1.5C_4H_8O_2$ (3.40 g, 10 mmol) was suspended in thf (40 cm³); $[NMe_2(CHCl)]Cl$ (1.27 g, 10 mmol) was added in portions over 0.5 h at 0 °C. The solution was then stirred for another 3 h while warming to room temperature. The thf was evaporated and the mixture extracted with warm hexane. Cooling to −30 °C afforded fawn *needles* (1.18 g).

Tricarbonyl(η-cyclopentadienyl)(dimethylaminomethylene)-vanadium(I) (12).—The complex $[V(\eta\text{-}C_5H_5)(CO)_4]$ (0.684 g, 3.0 mmol) was reduced by the method of Fischer [36] in thf (30 cm³) and decanted from the sodium amalgam. The salt $[NMe_2(CHCl)]Cl$ (0.381 g, 3.0 mmol) was added in portions at −20 °C over 0.5 h. The solution was stirred and warmed to room temperature over 3 h. The thf was then removed and the residue extracted with warm hexane. Fractional crystallisation from hexane at −30 °C separated the less-soluble $[V(\eta\text{-}C_5H_5)(CO)_4]$ from yellow *needles* (0.154 g).

Tricarbonyl(η-cyclopentadienyl)(dimethylaminomethylene)-molybdenum(II) *Tricarbonyl(η-cyclopentadienyl)molybdate*(0) (13).—The salt $Na[Mo(\eta\text{-}C_5H_5)(CO)_3]$ (10 mmol) was prepared from $[Mo(CO)_6]$ (2.64 g, 10 mmol) and $Na(C_5H_5)$ (12 mmol) by the method of King; [34] $[NMe_2(CHCl)]Cl$ (0.635 g, 5 mmol) was added and the mixture was stirred for 12 h at room temperature. The solution was filtered and diethyl ether added. On cooling to −30 °C, yellow *needles* crystallised (2.22 g).

Tricarbonyl(η-cyclopentadienyl)(dimethylaminomethylene)-tungsten(II) *Tricarbonyl(η-cyclopentadienyl)tungstate*(0) (14).—This complex was prepared in a similar manner to the molybdenum analogue, using 1,2-dimethoxyethane rather than thf as solvent.[37] Yellow *needles* were obtained (3.15 g).

Tricarbonyl(η-cyclopentadienyl)(dimethylaminomethylene)-molybdenum(II) *Tetrafluoroborate* (15).—To a solution of $Na[Mo(\eta\text{-}C_5H_5)(CO)_3]$ (10 mmol), prepared as above, was added $[NMe_2(CHCl)]Cl$ (1.27 g, 10 mmol) and the solution was stirred overnight. The thf was evaporated and CH_2Cl_2 (20 cm³), MeCN (20 cm³), and anhydrous $Na[BF_4]$ (3.5 g, 30 mmol) were added. The solution was stirred at room temperature for 2 h, evaporated to dryness, and CH_2Cl_2 (30 cm³) added. It was then filtered and thf (30 cm³) added. Cooling to −30 °C afforded yellow *crystals* (2.95 g). The *tungsten analogue* (16) was prepared similarly as yellow *crystals* (2.90 g).

cis-*Tetracarbonylchloro(dimethylaminomethylene)manganese*(I) (17).—To a solution of $[Mn_2(CO)_{10}]$ (1.95 g, 5 mmol) in thf (30 cm³) was added sodium amalgam (3 cm³, 1%).

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[34] R. B. King, ' Organometallic Syntheses,' Academic Press, New York, 1965, vol. 1.
[35] A. R. Manning, *J. Chem. Soc. (A)*, 1968, 1135.

[36] E. O. Fischer and R. J. J. Schneider, *Angew. Chem. Internat. Edn.*, 1967, **6**, 569.
[37] R. B. King and M. B. Bisnette, *J. Organometallic Chem.*, 1964, **2**, 15.

The solution was stirred vigorously at room temperature for 3 h, and filtered into a dropping funnel. It was then added dropwise to a suspension of $[NMe_2(CHCl)]Cl$ in thf (30 cm^3) over 1 h, stirred for another 3 h at room temperature, and filtered. Addition of hexane afforded yellow *octahedra* which were washed with water, dried, and recrystallised (0.574 g) from thf–hexane.

cis-*Tetracarbonylchloro(dimethylaminomethylene)rhenium*(I) (18).—This complex was prepared in a similar manner to (17) using $[Re_2(CO)_{10}]$ (1.0 g, 1.54 mmol). Fawn *crystals* were obtained (0.345 g).

Dicarbonylchloro(dimethylaminomethylene)(triphenylphosphine)cobalt(I) (19).—A suspension of $[Co_2(CO)_6(PPh_3)_2]$ (2.41 g, 3 mmol) was shaken with sodium amalgam (5 cm^3, 1%)in thf (30 cm^3). After 3 h a yellow solution of $Na[Co(CO)_3(PPh_3)]$ was obtained. This solution was filtered into a dropping funnel and added dropwise to a suspension of $[NMe_2(CHCl)]Cl$ (0.762 g, 6 mmol) in thf (20 cm^3). The solution was stirred for 0.5 h and filtered. Addition of diethyl ether and cooling to -30 °C afforded yellow *crystals* (1.26 g). *Bromodicarbonyl(dimethylaminomethylene)(triphenylphosphine)cobalt*(I) (20) was prepared similarly using $[Co_2(CO)_6(PPh_3)_2]$ (1.61 g, 2 mmol), $[NMe_2(CHBr)]Br$ (0.796 g, 4 mmol), and thf (50 cm^3). Yellow *crystals* were obtained (1.48 g).

Dichloro(dimethylaminomethylene)hydridobis(triphenylphosphine)rhodium(III) (30).—*Method* (a). The complex $[Rh\{CH(NMe_2)\}Cl_3(PPh_3)_2]$ (0.272 g, 0.344 mmol) and PPh_3 (1.3 g, 5 mmol) were heated under reflux in absolute ethanol for 5 h, when a yellow precipitate had formed. The mixture was cooled and diethyl ether added to complete precipitation of the solid. The pale yellow *solid* was filtered off and washed several times with diethyl ether and dried *in vacuo* (0.250 g).

Method (b). To a suspension of $[\{Rh[CH(NMe_2)](CO)Cl_3\}_2]$ (1.009 g, 1.715 mmol) in absolute ethanol was added PPh_3 (0.5 g, 25 mmol) and the mixture was heated. Evolution of gas immediately occurred and the orange precipitate became bright yellow. The mixture was heated under

reflux for 1 h; after cooling, the solid was filtered off, washed in diethyl ether and then several times with warm benzene. The benzene washings, after reduction in volume and addition of hexane, afforded yellow crystals (0.801 g), identified by their i.r. spectrum. The benzene–insoluble residue was identified as the required *product* (1.182 g).

Dichloro(dimethylaminomethylene)hydridobis(triethylphosphine)rhodium(III) (31).—A suspension of (30) (0.483 g, 0.638 mmol) in benzene and triethylphosphine (0.15 cm^3, 1.4 mmol) were boiled under reflux for 30 min until a clear orange solution was obtained. After cooling, the solvent was removed *in vacuo* and the yellow-orange residue washed several times with hexane. Yellow-orange *crystals* (0.269 g) were obtained from chloroform–hexane.

Dichloro(dimethylaminomethylene)hydridobis(dimethylphenylphosphine)rhodium(III) (32).—A suspension of (30) (0.231 g, 0.306 mmol) in benzene and dimethylphenylphosphine (0.2 cm^3, 1.5 mmol) was boiled under reflux for 30 min to obtain a clear yellow solution. After cooling, the solvent was removed *in vacuo* and the oily orange residue washed in diethyl ether to obtain a pale yellow solid which, after recrystallisation from chloroform–hexane, gave the required *product* (0.202 g).

trans-*Carbonylchlorobis(1,3-dimethylimidazolidin-2-ylidene)rhodium*(I).—To a suspension of $[\{Rh[CH(NMe_2)](CO)Cl_3\}_2]$ (0.295 g, 0.50 mmol) in thf (25 cm^3) was added bi(1,3-dimethylimidazolidin-2-ylidene) (0.40 g, 2 mmol). The solution was heated under reflux for 1 h, cooled, and filtered. Addition of diethyl ether and cooling to -30 °C afforded pale yellow *crystals* [25,38] (0.218 g, 60%).

[38] M. J. Doyle, D. Phil. Thesis, University of Sussex, 1974.