Carbene Complexes. Part VIII.[1] Chromium(0), Iron(0), Rhodium(I), Iridium(I), Nickel(II), Palladium(II), Platinum(II), and Gold(I) Mono- and Oligo-carbene Species from Electron-rich Olefins

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The reaction of the electron-rich olefin 1,1′,3,3′-tetramethyl-2,2′-bi-imidazolidinylidene (I) ($\equiv L_2$) or, in one case, of bis(*N*-methylbenzothiazolinylidene) (II) ($\equiv L'_2$) with various transition metal d^6 or d^8 complexes yields mono-di-, or tri-carbene metal complexes of Cr^0, Fe^0, Rh^I, Ir^I, Ni^{II}, Pd^{II}, Pt^{II}, or Au^I, such as *cis*-$Cr(CO)_4(L)_2$, $[Ir(CO)(L)_3]^+$, or *cis*-$[PtMe(PPh_3)(L)_2]^+$. The reactions involve (i) displacement from the metal of a negative (Cl^-, I^-) or neutral [CO, tertiary phosphine, or π-allyl (transformed into σ-allyl)] ligand or ligands by one or more nucleophilic carbene moieties L or L′, (ii), for $[Rh(CO)_2Cl]_2$, bridge-splitting by L, or (iii) displacement of a halide anion by BF_4^-. The twenty-four new carbene complexes are stable and their ready formation in high yield serves as a further demonstration of the scope of electron-rich olefins as reagents in transition metal chemistry. They clearly behave as nucleophilic carbene (L or L′) transfer reagents.

In Parts I [2] and II,[3] we reported that an electron-rich olefin such as (I) ($\equiv L_2$) or (II) ($\equiv L'_2$) cleaves the dihalide bridge of a binuclear Pd^{II} or Pt^{II} species, such as $M_2Cl_4(PEt_3)_2$, to yield the carbene complex, *trans*-$MCl_2(PEt_3)L$(or L′) or its *cis*-isomer. Some Rh^I mono-carbene derivatives, $RhCl(Q)PPh_3[C\{N(R)CH_2\}_2]$ ($Q = PPh_3$ and $R = Ph$; $Q = CO$ and $R = Ph$; $Q = PPh_3$ and $R = p\text{-}Me{\cdot}C_6H_4$), were isolated from related olefins [the *NN′N″N‴*-tetraphenyl or -tetra-*p*-tolyl analogues of (I), taking this as the tetramethyl-compound] and $RhCl(PPh_3)_3$ or $RhCl(CO)(PPh_3)_2$.[4]

Prior to our preliminary publication,[5] carbene complexes of Ir^I and Ni^{II} were unknown;[6] likewise, although a tetra- (Pt^{II}) and some di- (Cr^0, W^0, Fe^{II}, Pd^{II}, Pt^{II}, and Hg^{II}) carbene complexes had been described, the tricarbene complexes (III), (XIII), and (XV) represented a new genus; recently an Os^{II} tricarbene complex has

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[1] Part VII, B. Çetinkaya, M. F. Lappert, G. M. McLaughlin, and K. Turner, *J.C.S. Dalton*, 1974, 1591.

[2] Part I, D. J. Cardin, B. Çetinkaya, E. Çetinkaya, and M. F. Lappert, *J.C.S. Dalton*, 1973, 514.

[3] Part II, B. Çetinkaya, E. Çetinkaya, and M. F. Lappert, *J.C.S. Dalton*, 1973, 906.

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

[5] B. Çetinkaya, P. Dixneuf, and M. F. Lappert, *J.C.S. Chem. Comm.*, 1973, 206.

[6] *Cf.* D. J. Cardin, B. Çetinkaya, and M. F. Lappert, *Chem. Rev.*, 1972, **72**, 545; F. A. Cotton and C. M. Lukehart, *Progr. Inorg. Chem.*, 1972, **16**, 487.

been characterised[7] (see also ref. 8 for Rh^{I}). An attempt to obtain a π-olefin derivative of Cr^{0} by heating $Cr(CO)_5[C(NMe_2)Ph]$ afforded the substituted ethylenediamine chelate $Cr(CO)_4(NMe_2CHPh)_2$.[9] This is somewhat surprising, because carbene metal derivatives frequently yield the olefin (dimer of the carbene moiety) upon pyrolysis.[6,10] Similar reactions have been cited in support of the hypothesis that free carbenes are reaction intermediates. More convincing evidence, although not conclusive, derives from trapping experiments, *e.g.*, with *trans*-methyl crotonate[11] or silanes (*e.g.*, Et_3SiH or Ph_2SiH_2).[9,12] It will be necessary to show that the products of trapping do not arise from the free electron-rich olefin. Although the latter does not dissociate into its constituent carbene moieties, it may do so in the presence of a suitable transition metal derivative.[4]

TABLE 1

Cr^{0}, Fe^{0}, Rh^{I}, Ir^{I}, Au^{I}, Ni^{II}, Pd^{II}, or Pt^{II} mono- and oligo-carbene species from the electron-rich olefins (I) ($\equiv L_2$) or (II) ($\equiv L'_2$), and their characterisation ($P = PPh_3$, $P' = PPhMe_2$, $P'' = PPhEt_2$, $P''' = PEt_3$)

Compound	No.	Yield (%)	M.p. (t/°C)	Colour of crystals	Found (Required) (%)		
					C	H	N
$[Ir(CO)L_3]^+BF_4^-$	(III)	77	204—206	Yellow	32·7 (31·9)	5·1 (5·0)	13·8 (13·9)
$[Ir(CO)P_2L]^+BF_4^-$	(IV)	94	225—228 (dec.)	Yellow–orange	53·7 (54·2)	4·5 (4·3)	3·5 (3·3)
$Ir[N{:}C(CF_3)_2](CO)PL$	(V)	62	153—155	Yellow–orange	44·0 (43·6)	3·5 (3·4)	5·7 (5·7)
trans-$RhCl(CO)L_2$ [c]	(VI)	51	*ca.* 205 [a] (dec.)	Yellow	36·7 (36·4)	5·7 (5·5)	15·3 (15·4) [b]
$AuClL_2$ [d]	(VII)	84	270 (dec.)	White	28·7 (27·9)	4·8 (4·7)	13·0 (13·0)
$[AuL_2]^+BF_4^-$	(VIII)	90	218—225	White	24·9 (25·0)	4·2 (4·2)	11·1 (11·6)
cis-$Cr(CO)_4L_2$	(IX)	53 [e] 72 [f]	235—237 [a]	Yellow	46·1 (46·7)	5·7 (5·6)	15·5 (15·6)
$Fe(CO)_4L$ [g]	(X)	77	48—50	Yellow	40·3 (40·6)	3·8 (3·8)	10·6 (10·5)
trans-$RhCl(CO)L'_2$	(XI)	32	*ca.* 210 [a] (dec.)	Yellow	43·8 (43·9)	3·2 (3·0)	6·3 (6·0)
trans-$[NiCl(P'')L_2]^+VF_4^-$	(XII)	70	140—145 (dec.)	Yellow	43·6 (44·2)	6·7 (6·5)	8·1 (10·3)
$[NiClL_3]^+BF_4^-$	(XIII)	49	120—160 (dec.)	Yellow	36·8 (37·9)	6·5 (6·4)	16·2 (17·7)
trans-$[PdCl(P''')_2L]^+BF_4^-$	(XIV)	90	192—196	White	36·6 (36·2)	7·2(7·1)	6·3 (5·0)
$[PtHL_3]^+BF_4^-$	(XV)	80	183—185	White	32·0 (31·2)	5·7 (5·4)	14·4 (14·5)
$[PtClL_3]^+BF_4^-$	(XVI)	90	244—246	White	30·1 (29·4)	5·2 (4·9)	13·7 (13·7)
cis-$[PtMe_2(P)L]$	(XVII)	71	213—214	White	51·1 (51·3)	5·3 (5·3)	4·9 (4·8)
cis-$[PtMe_2(P')L]$	(XVIII)	90	129—130	White	39·3 (39·0)	6·1 (5·9)	6·1 (6·1)
cis-$[PtCl(P)L_2]^+Cl^-$	(XIX)	82	266—268	White	45·8 (46·4)	5·0 (4·9)	7·7 (7·7)
cis-$[PtCl(P)L_2]^+BF_4^-$	(XX)	67	264—265	White	43·6 (43·4)	4·6 (4·6)	7·2 (7·2)
cis-$[PtMe(P)L_2]^+I^-$	(XXIII)	50	214—218	White	43·2 (43·8)	4·8 (4·8)	7·0 (7·1)
$Pt(\sigma\text{-}C_3H_5)Cl(P)L$	(XXIV)	67	190—193	White	50·0 (49·4)	4·9 (4·8)	4·5 (4·4)
cis-$[Pt(\sigma\text{-}C_3H_5)(P)L_2]^+Cl^-$	(XXV)	61		White	49·9 (51·0)	5·6 (5·5)	7·7 (7·7)
cis-$[Pt(\sigma\text{-}C_3H_5)(P)L_2]^+BF_4^-$	(XXVI)			White	45·9 (47·6)	5·3 (5·2)	6·6 (7·2)

[a] Decomposition begins at *ca.* 175°. [b] Found: M, 359 (isopiestic in benzene) (Required: M, 363). [c] Also forms $[Rh(CO)L_3]^+Cl^-$, according to ^{1}H n.m.r. [d] Hygroscopic. [e] From $Cr(CO)_6$. [f] From *cis*-$Cr(CO)_4(NCMe)_2$. [g] Decomposes in chlorinated solvents; air-sensitive.

TABLE 2

Selected spectroscopic data on carbene complexes (III)—(XI)

Compound	^{1}H n.m.r.[a]			I.r. (ν_{max} cm^{-1}) [b] (assignment in parentheses)		
	τ(Me)	$\tau(CH_2)$	Solvent	ν(CO)	ν(CN)	Others
(III)	6·80,[c] 6·98 [d]	6·41,[c] 6·50 [d]	$CDCl_3$	1960vs	1500s	
(IV)	7·45	7·25	$CDCl_3$	1980vs	1530m, 1505m	
(V) [e]	6·70	6·52	$CDCl_3$	1935vs	1525s	
(VI)	6·50	6·38	$CDCl_3$	1925vs	1515vs	290s (RhCl)
(VII)	6·80	6·20	$CDCl_3$		1540s, 1515sh	
(VIII) [f]	6·80	6·24	$CDCl_3$		1540s, 1515sh	
(IX) [g]	6·78	6·54	$CDCl_3$	1990s, 1885s, 1850s, 1830sh [h]		
(X) [i]	7·05 [j]	7·60 [j]	C_6D_6	2044s, 1963s, 1938vs [k]		
(XI)	5·33		$CDCl_3$	1935	1525s	

[a] Signals are singlets, unless otherwise stated. [b] Nujol mull. [c] Assigned to two *trans*-L groups. [d] Assigned to a *cis*-L group (on basis of integrated intensities). [e] ^{19}F N.m.r. gives a doublet at $\delta = 70{\cdot}0$ p.p.m. in $CHCl_3$ (rel. to $CFCl_3$), $J(^{31}P^{19}F) = 1{\cdot}75$ Hz. [f] Much less soluble than (VII). [g] ^{1}H n.m.r. and i.r. data similar to $Cr(CO)_4[C(NMeCH{:})_2]_2$. [h] In $CHCl_3$. [i] ^{1}H N.m.r. shows complex peaks with CCl_4. [j] Doublet. [k] In n-C_6H_{14}.

Another type of experiment from which participation of carbene intermediates might be inferred is the ' carbene transfer ' procedure.[6] This was first demonstrated for the system of equation (1).[13] Another example is the pyrolysis or photolysis reaction (2).[14] In the light of (a)

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the present demonstration of formation of mono- (X) and di- (IX) carbene complexes of Fe^0 and Cr^0, respectively from $Fe(CO)_5$ and $Cr(CO)_6$, and (b) olefin formation from carbene complexes,[4,10] the possibility of electron-rich olefin intermediates in such ' carbene transfer ' reactions is very real.

$$Mo(\pi\text{-}C_5H_5)NO(CO)[C(OMe)Ph] + Fe(CO)_5 \xrightarrow{h\nu} Fe(CO)_4[C(OMe)Ph] + Mo(\pi\text{-}C_5H_5)NO(CO)_2 \quad (1)$$

$$Cr(CO)_5[C\{N(Me)CH{:}\}_2] \xrightarrow{h\nu \text{ or } kT} Cr(CO)_4[C\{N(Me)CH{:}\}_2]_2 \ (8\%) \quad (2)$$

The formation of the Au^I complex $[AuL_2]^+Cl^-$, (VII), from the neutral precursor $AuCl(PPh_3)$, has some precedent in the observation that the latter reacts with triphenylphosphine to yield $[Au(PPh_3)_2]^+Cl^-$.[15]

acetonitrile or triphenylphosphine.[16] The *trans*-configuration for compound (V) is suggested because the ^{19}F n.m.r. spectrum shows $J(^{31}P^{19}F)$ appropriate for *cis*-coupling,[17] and ν(CO) is similar to that found [17] for *trans*-$Ir[N{:}C(CF_3)_2](CO)(PPh_3)_2$ [see also *trans*-$Rh\{N{:}C(CF_3)_2\}P_2L$, for which *X*-ray analysis establishes the geometry [18]]. An unexpected feature is the observation of doublet signals for each of CH_3 and CH_2 in $Fe(CO)_4L$, (X). A possible explanation is that there is fluxional behaviour with slow exchange on the ^1H n.m.r. time scale of equatorial and axial sites for L, or alternatively that there is substantial distortion. A corresponding dedihydro-complex $(OC)_4Fe[C(NMeCH{:})_2]$ has been prepared [19] and characterised by single crystal *X*-ray analysis; [20] the carbene ligand occupies an axial site, but there is considerable deviation from a trigonal bipyramid.

TABLE 3

Selected spectroscopic data on carbene complexes (XII)—(XXVI)

	^1H n.m.r.[a]			I.r. (ν_{max}, cm^{-1})[b] (assignment in parentheses)		
Compound	τ(Me)	$τ(CH_2)$	Solvent	ν(MCl)	ν(CN)	Others
(XII)	6·8[c]	6·0[c]	$CDCl_3$	310	1525	
(XIII)	6·45,[d] 6·80[e]	6·0,[d] 6·4[e]	$CDCl_3$	315	1515	
(XIV)[f]	6·60	6·10	$CDCl_3$	305	1520	
(XV)[g]	6·68,[i] 6·80[h]	6·27[h]	$(CD_3)_2CO$		1510	1985 [ν(PtH)]
(XVI)	6·66,[i] 6·80[i]	6·35[h]	$CDCl_3$	305	1515	
(XVII)[j]	7·07	6·95[h]	$CDCl_3$		1500	538 [ν(PtC)]
(XVIII)[k]	6·97	6·27[h]	$CDCl_3$		1495	525 [ν(PtC)]
(XIX)	6·55,[i] 6·95[i]	?	$CDCl_3$	310	1535	
(XX)	6·60,[i] 7·00[i]	?	$CDCl_3$	320	1530	
(XXI)[l]	7·04[i]	6·80	$CDCl_3$	310	1525	
(XXIII)[m]	6·67,[i] 7·07[i]	?	$CDCl_3$		1510	538 [ν(PtC)]
(XXIV)	7·16, 7·30	?	$CDCl_3$	300	1520	532 [ν(PtC)], 1608 [ν(C:C)]
(XXV)[n]	6·70, 7·03	?	$CDCl_3$		1510	540 [ν(PtC)], 1608 [ν(C:C)]
(XXVI)[o]	6·70, 7·05	?	$CDCl_3$		1515	535 [ν(PtC)], 1610 [ν(C:C)]

[a] Singlet, unless otherwise stated. [b] Nujol mull. [c] Multiplet, not a clean spectrum, possibly impure (see analytical data of Table 1). [d] Assigned to a *cis*-L group. [e] Assigned to two *trans*-L groups, on basis of integrated intensities. [f] PEt_3 ^1H N.m.r. signals at τ 8·10 and 8·75. [g] $^5J(^{195}PtNC^1H_3)$ 4·0 Hz, $^2J(^{195}Pt^1H)$ 912 Hz, Pt*H* τ 17·48. [h] Complex multiplet. [i] Triplet due to Pt coupling of NMe. $^5J(^{195}PtNC^1H_3)$ 4—6 Hz. [j] ^1H N.m.r.: *Me*Pt-P (*trans* and *cis*, respectively): τ(Me) = 9·99 and 9·83; $^4J(^{31}PPtC^1H_3)$ = 8·0 and 7·5 Hz; $^3J(^{195}PtC^1H_3)$ = 60·5 and 70·7 Hz. [k] ^1H N.m.r.: PMe_2, τ 8·40; $^3J(^{31}PC^1H_3)$ 7·7 Hz; $^4J(^{195}PtPC^1H_3)$ 22·2 Hz; *Me*Pt-P (*trans* and *cis*, respectively): (Me) τ 9·87 and 9·83; $^4J(^{31}PPtC^1H_3)$ 8·8 and 7·5 Hz; $^3J(^{195}PtC^1H_3)$ 61·0 and 71·0 Hz; spectrum essentially the same in C_6D_6, except that $(PtC^1H_3$ is at τ 9·07 and 9·03, for *trans* and *cis* respectively. [l] ^1H N.m.r.: PMe_2, 8·04 [triplet of triplets: $^3J(^{31}PC^1H_3)$ 7·5 Hz, $^4J(^{195}PtC^1H_3)$ 28·5 Hz]. [m] ^1H N.m.r.: PtMe τ 10·09 [$^4J(^{31}PPtC^1H_3)$ 7·5 Hz; $^3J(^{195}PtC^1H_3)$ 56·0 Hz]. [n] ^1H N.m.r.: (CH_2Pt) τ 8·30 (?); hygroscopic (i.r.). [o] ^1H N.m.r.: (CH_2Pt) τ 8·82 (?).

Data for the new carbene complexes are in Tables 1—3. For those species in which the possibility of isomerism exists, our assignments of Schemes 1 and 2 rely on spectroscopic data (Tables 2 and 3). It is clear from the ^1H n.m.r. results on the tricarbene Ir^I complex (III) that the CH_2 and CH_3 protons of the carbene ligand L are distinguishable for *cis*- and *trans*-positions (it may be that this is due to a different *trans*-influence for CO and L in Ir^I). On this basis, the dicarbene complexes of Rh^I and Ir^I are taken as having the *trans*-configuration (no splitting of CH_2 or CH_3 signals), and the Cr^0 as the *cis*-complex. Because the ligand L is not particularly bulky, the latter result is not unexpected, by analogy for example with the formation of *cis*-complexes using The n.m.r. spectrum of this complex shows singlet C^1H_3 and C^1H signals.[19] The ^{13}C n.m.r. spectrum of (X) does not show splittings of $^{13}CH_3$ or $^{13}CH_2$.[21]

In several of the reactions illustrated in Schemes 1 and 2, there is a choice of ligands which may be displaced by carbene. However, there is no unique pattern for their relative migratory aptitudes: *viz.*, $Cl^- > P$ (Ir), P > CO (Ir), and $Cl^- >$ CO (Ir) but CO > Cl^- (Rh). The Cl^-/CO results are not likely to be attributable to *trans*-effects, since bridge-splitting affords *cis*-$RhCl(CO)_2P$, as the kinetically-controlled precursor to (VI), or (XI), which like *trans*-$IrCl(CO)P_2$ has chloride and CO mutually *trans*.

In our preliminary publication we showed that electron-rich olefins have an extensive transition metal

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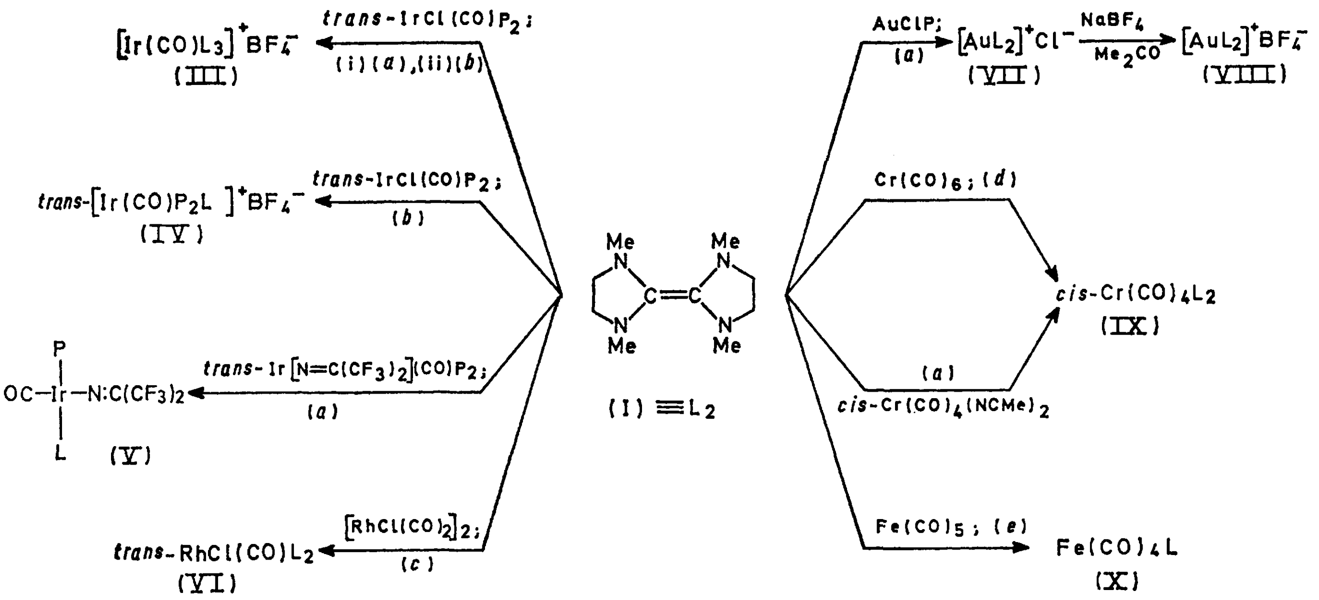
[18] M. J. Doyle, M. F. Lappert, G. M. McLaughlin, and J. McMeeking, *J.C.S. Dalton*, 1974, 1494.

[19] K. Öfele and C. G. Kreiter, *Chem. Ber.*, 1972, **105**, 529.

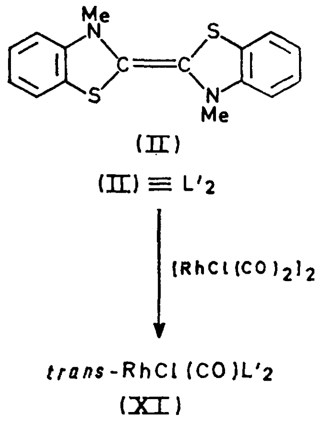
[20] G. Huttner and W. Gartzke, *Chem. Ber.*, 1972, **105**, 2714.

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

chemistry.[5] Although they do not spontaneously dissociate in solution into carbene moieties,[4] in the presence of the appropriate metal complex they nevertheless behave essentially in this way and thus have a ligand chemistry not dissimilar to that of tertiary phosphines. This analogy was pursued above for mono-, di-, or tricarbene complexes of Cr^0, Fe^0, Rh^I, Ir^I, and Au^I, illustrated by reactions involving displacement from the metal of Cl^-, CO, or tertiary phosphine. Such chemistry is also characteristic of some Group VIIIc complexes. Previously, we disclosed briefly four such reactions.[5] Details and extensions are now provided for fourteen systems. This has led to the new compounds (XII)—(XXVI) (see Scheme 3), details for which are in Tables 1 and 3. Carbene complexes of Group VIIIc metals have also been accessible from corresponding isonitrile [22] or acetylene [23] (for cationic complexes, which may also be regarded as metallocarbonium ions) complexes.[6] Our procedure for obtaining cationic complexes, especially tetrafluoroborates, may be compared with those used for cationic isonitrile derivatives of Group VIIIc metals: [24] complexes MCl_2Q_2 (Q is, for example, a tertiary phosphine) were treated with isocyanide in presence of a silver salt of a non-co-ordinating anion, *e.g.*, $AgBF_4$, in order to eliminate Cl^- as AgCl. It is clear, by comparison, that the cationic carbene complexes are, in general, much more stable than isonitrile or phosphine analogues because the equilibria such as $MCl_2Q_2 + L' \rightleftharpoons [MClQ_2L']^+Cl^-$ invariably favour the ionic product for L′ = the nucleophilic carbene ligand. This may, however, be due to solubility factors.



SCHEME 1 Some transition metal complex reactions of the electron-rich olefin (I) (≡ L_2) (P = PPh_3). Reaction conditions: (*a*) PhMe, reflux, 5—20 min; (*b*) Me_2CO, $NaBF_4$, reflux, 3 h; (*c*) DMF, 110°, 15—20 min; (*d*) THF, hν, 20°, 8 h; (*e*) PhH, reflux, ½ h



SCHEME 2 A transition metal complex reaction of the electron-rich olefin (II) (≡ L'_2) (in DMF at 120° for 10 min)

Of the reactions shown in Scheme 3, the conversion of the bihapto-π-allyl into the monohapto-σ-allyl ligand with concomitant occupation by a carbene ligand of the vacated co-ordination site around platinum [*cf.*, formation of (XXIV)—(XXVI)] is the only new reaction type for an electron-rich olefin, such as (I) (similar π- ⟶ σ-allyl rearrangements have been studied for other ligands [25]). The other types involve displacement of phosphine and/or chloride and show differences of phosphine lability depending on the phosphine or the metal. For neutral complexes it appears that the migratory aptitude of chloride or iodide is greater than that of a tertiary phosphine [*cf.* the formation of (XIV), (XXI)—(XXIII)]; whereas the formation of (XII), (XIII), and

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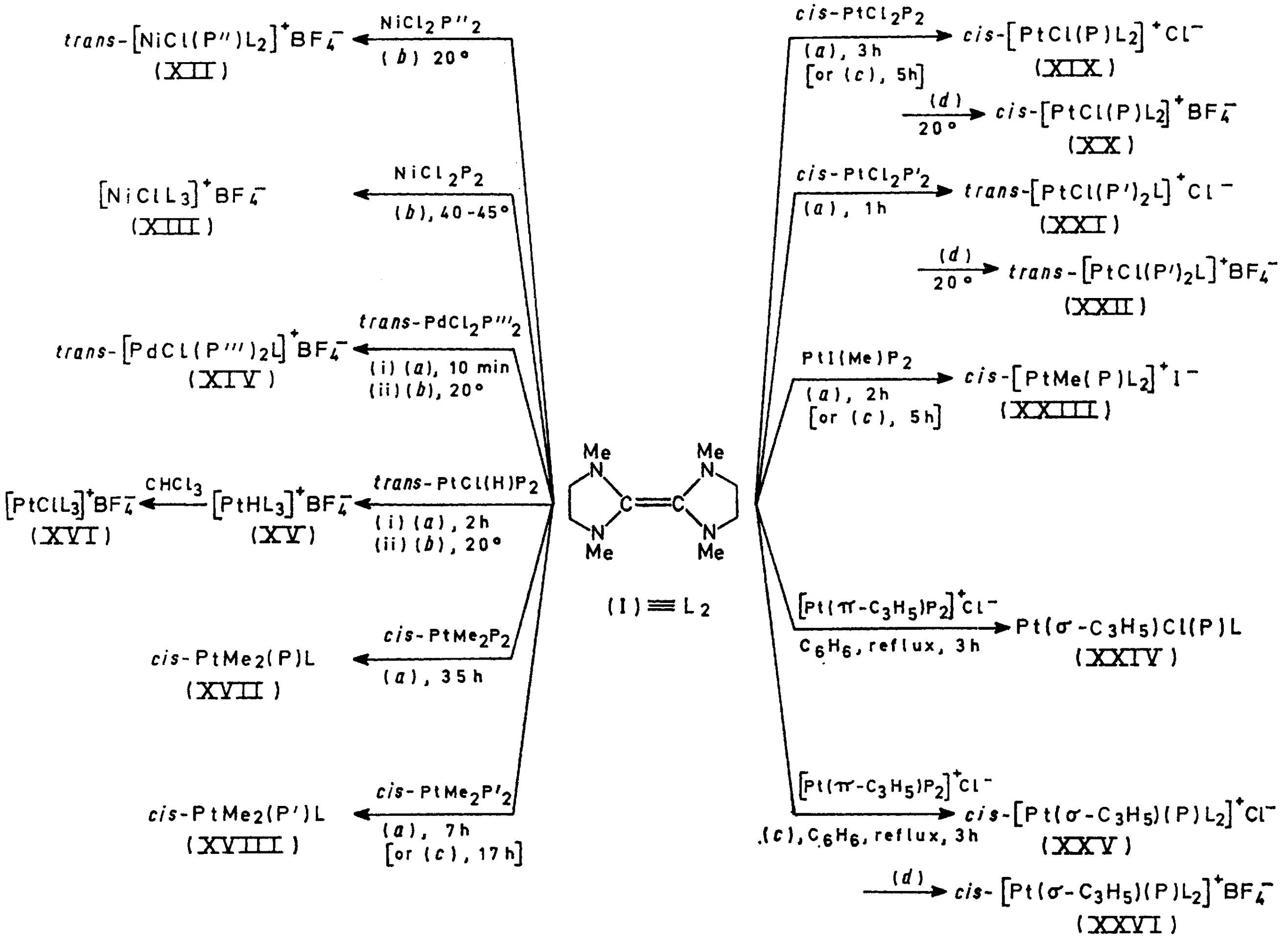
[24] W. J. Cherwinski, H. C. Clark, and E. L. Manzer, *Inorg. Chem.*, 1972, **11**, 1511.

[25] *Cf.*, M. Tsutsui, M. Hancock, J. Ariyoshi, and M. N. Levy, *Angew. Chem. Internat. Edn.*, 1967, **8**, 410.

(XIX) suggests the reverse order for some cationic complexes. By monitoring reactions leading to neutral (XVII) or (XVIII), using ^{1}H n.m.r., it is clear that phosphine displacement lability is greater for PMe_2Ph than PPh_3; but, by comparing reactions leading to the cationic complexes (XII) and (XIII) or (XIX) and (XXI), the alkylphosphine is less readily displaced than PPh_3. Comparison of MCl_2P_2 reactions reveals that ease of phosphine displacement decreases in the sequence Ni > Pd ≈ Pt [*cf.* (XIII) and (XIX), (XII) and (XXI), (XIV) and (XXI)]. From Schemes 1 or 3 it is further noted that (a) H, Me, σ-C_3H_5, or $(CF_3)_2C{:}N$ are not directly displaced from the metal co-ordination sphere [*cf.* (V), (XVII), (XVIII), (XXIII)—(XXV)]; (b) that for Pt^{II}, the presence of Me, σ-C_3H_5, or Cl favours the formation of a dicarbene cationic complex in which the two carbene ligands are mutually cisoid [*cf.* (XIX), (XXIII), and (XXV)]; and (c) the formation of a tricarbene complex is favoured by a fourth ligand which is strongly electronegative [*cf.* (III) or (XIII)].

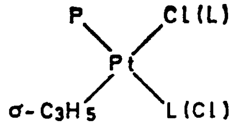


SCHEME 3 Some Group VIIIc metal complex reactions of the electron-rich olefin (I) (≡ L_2) (P = PPh_3, P′ = $PPhMe_2$, P″ = $PPhEt_2$ P‴ = PEt_3). Reaction conditions: (*a*) PhMe, reflux, (*b*) Me_2CO, $NaBF_4$, (*c*) excess of olefin, (*d*) H_2O, $NaBF_4$, 20°

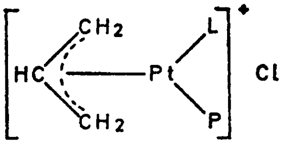
Reactions in Scheme 3 which do not involve olefins relate to anion (Cl^-/BF_4^-) exchange, and the conversion of a hydridoplatinum(II) complex (XV) into the corresponding chloroplatinum(II) species (XVI), by treatment with chloroform.

All the new complexes are stable, although of the ionic compounds the chlorides, unlike the tetrafluoroborates, are hygroscopic. Assignment of structure and stereochemistry is based on analysis, spectroscopic data (see Table 3), and comparisons with results earlier reported. It appears that for di- or tri-carbene complexes, mutually *cis*-carbene ligands are distinguished by separate NCH_3 ^{1}H n.m.r. signals. The least definite assignments relate to compounds (XIII) (because of impurity), (XIX), (XX), and (XXIV). With respect to (XIX) and (XX) (PPh_3 complexes), the *cis*-configuration is suggested by the ^{1}H n.m.r. NCH_3 signals. Because of our assignment of *cis*-configuration for compounds (XXV) and (XXVI), and because of the presence of Pt–Cl and C=C i.r. bands for (XXIV), it is likely that (XXIV) is one of two stereoisomers, (XXVII), rather than the isomeric π-allyl ionic (XXVIII).

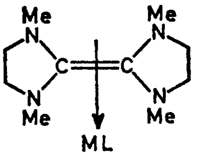
The demonstration that electron-rich olefins readily displace neutral or anionic ligands from a transition metal centre suggests (i) that these olefins are potentially useful reagents in complex chemistry and (ii) that a wide range of corresponding carbene complexes becomes accessible. The mechanism of the reactions may involve an intermediate π-complex, such as (XXIX), which could decompose bimolecularly to yield the carbene metal complex and olefin, or unimolecularly to yield the former and the nucleophilic carbene L (see also refs. 1, 4, and 26).



(XXVII)



(XXVIII)



(XXIX)

EXPERIMENTAL

General procedures have been described previously.[1]

Reactions of 1,1′,3,3′-*Tetramethyl*-2,2′-*bi-imidazolidinylidene*.—(a) *With hexacarbonylchromium*(0). A solution of the olefin (0·5 ml) and the hexacarbonyl (0·4400 g, 2·99 mmol) in tetrahydrofuran (THF) (150 ml) was irradiated, for 8 h, using a Hanovia lamp, whereafter the solvent was evaporated. The residue was heated (*ca.* 100°) for ½ h to sublime unreacted hexacarbonyl. The involatile part was dissolved in THF (20 ml) and was precipitated by adding n-hexane (20 ml) to obtain *bis*(1,3-*dimethylimidazolidin*-2-*ylidene*)*tetracarbonylchromium*(0) (0·383 g, 53%).

(b) *With bis*(*acetonitrile*)*tetracarbonylchromium*(0).[16] Hexacarbonylchromium(0) (0·289 g, 1·32 mmol) was heated in acetonitrile (*ca.* 10 ml) for 9 h. Volatiles were removed and the residue was dissolved in toluene (15 ml). This solution was heated with the olefin (0·4 ml) under reflux for ½ h. On cooling (−20°), yellow crystals were deposited. Reprecipitation from THF (15 ml) by addition of n-hexane (20 ml) afforded bis(1,3-dimethylimidazolidin-2-ylidene)-tetracarbonylchromium(0) (0·340 g, 72%).

(c) *With pentacarbonyliron*(0). A solution of the pentacarbonyl (0·35 ml, 2·60 mmol) and the olefin (0·3 ml) in benzene (25 ml) was heated (½ h) under reflux. The colour of the solution gradually became darker and a solid separated. The volume of the solution was reduced to 2 ml and n-hexane (25 ml) was added. The brownish solid was filtered off. Upon cooling (−20°), the filtrate gave crystals of (1,3-*dimethylimidazolidin*-2-*ylidene*)*tetracarbonyliron*(0) (0·530 g, 77%).

(d) *With di*-μ-*chloro-tetracarbonyldirhodium*(I).[27] To a solution of the rhodium complex (0·248 g, 1·27 mmol) in *NN*-dimethylformamide (DMF) (5 ml) was added the olefin (0·3 ml). A dark precipitate was formed. The mixture was slowly heated to 120° and held there for 15 min. Volatiles were removed under reduced pressure and the residue was treated with hot benzene (30 ml) to give a yellow filtrate which was concentrated to *ca.* 3 ml. Diethyl ether was added to precipitate trans-*chlorocarbonylbis*(1,3-*dimethylimidazolidinylidene*)*rhodium*(I) (0·233 g, 50%).

(e) *With* trans-[*bis*(*trifluoromethyl*)*methyleneamido*]*carbonylbis*(*triphenylphosphine*)*iridium*(I).[17] The iridium complex (0·626 g, 0·69 mmol) and the olefin (0·25 ml) were heated in toluene under reflux for 20 min. The solvent was removed *in vacuo* to give an oily residue, which was dissolved in ether (5 ml) and filtered. Addition of n-hexane to the filtrate gave crystals of *carbonyl*[*bis*(*trifluoromethyl*)-*methyleneamido*](*triphenylphosphine*)(1,3-*dimethylimidazolidin*-2-*ylidene*)*iridium*(I) (0·320 g, 62%).

(f) *With* trans-*chlorocarbonylbis*(*triphenylphosphine*)*iridium*(I)[28] *in the presence of sodium tetrafluoroborate*. To a stirred solution/suspension of the iridium compound (0·390 g, 0·50 mmol) and sodium tetrafluoroborate (0·060 g, 0·54 mmol) in acetone (25 ml) was added the olefin (0·25 ml). The mixture was heated under reflux for 3 h. The solvent was removed and the oily residue was washed with n-hexane (15 ml). The yellow precipitate was dissolved in dichloromethane (10 ml) and filtered. Upon adding ether (10 ml), the filtrate gave crystals of *carbonyl*(1,3-*dimethylimidazolidin*-2-*ylidene*)*bis*(*triphenylphosphine*)*iridium*(I) *tetrafluoroborate* (0·435 g, 94%).

(g) *With* trans-*chlorocarbonylbis*(*triphenylphosphine*)*iridium*(I). Upon adding the olefin (0·4 ml) to a warm suspension of the iridium compound (0·703 g, 0·90 mmol) in toluene (25 ml) first a clear solution and then an orange precipitate formed. The mixture was heated (10 min) under reflux and was allowed to cool to 20°. The precipitate (0·512 g) was filtered off, redissolved in acetone (20 ml), and stirred (1 h) with sodium tetrafluoroborate (0·130 g) at 20°. The solvent was removed and the residue was treated with dichloromethane (15 ml). The filtrate was concentrated to *ca.* 5 ml and ether (15 ml) was added to obtain *carbonyltris*(1,3-*dimethylimidazolidin*-2-*ylidene*)*iridium*(I) *tetrafluoroborate* (0·464 g, 77%).

(h) *With chlorotriphenylphosphinegold*(I).[15] A mixture of the olefin (0·25 ml) and the gold complex (0·495 g, 1·00 mmol) was slowly heated in toluene (20 ml). At about 100°, a pale yellow solution formed. Upon further heating (5 min, at reflux temperature) a white precipitate separated. The mixture was cooled to 20°, the solid filtered off and washed with n-hexane (20 ml) to give hygroscopic *bis*(1,3-*dimethylimidazolidin*-2-*ylidene*)*gold*(I) *chloride* (0·360 g, 84%).

This anionic complex (0·215 g, 0·50 mmol) was treated with sodium tetrafluoroborate (0·110 g, 1·00 mmol) in acetone (20 ml) at 40—50° for 20°. The solvent was removed and dichloromethane (20 ml) added to the residue. Filtration and addition of ether gave *bis*(1,3-*dimethylimidazolidin*-2-*ylidene*)*gold*(I) *tetrafluoroborate* (0·216 g, 90%).

Reaction of Bis(N-*methylbenzothiazolinylidene*) *with Di*-μ-*chloro-tetracarbonyldirhodium*(I).—A solution of the rhodium complex (0·500 g, 1·27 mmol) and the olefin (0·76 g, 2·55

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[26] D. J. Cardin, B. Çetinkaya, M. J. Doyle, and M. F. Lappert, *Chem. Soc. Rev.*, 1973, **2**, 99.

[27] J. A. McCleverty and G. Wilkinson, *Inorg. Synth.*, 1966, **8**, 211.

[28] J. P. Collman, C. T. Sears, and M. Kubota, *Inorg. Synth.*, 1968, **11**, 101.

mmol) in DMF (8 ml) was slowly heated. The temperature was held at 100—120° for 10 min. A brown solution formed. This was allowed to cool to 20°, while a crystalline solid separated out which was filtered off, washed with ether (15 ml), and dried to yield *chlorocarbonylbis*(N-*methylbenzothiazolinylidene*)*rhodium*(I) (0·3973 g, 32%).

Reactions of 1,1′,3,3′-*Tetramethyl*-2,2′-*imidazolidinylidene*, (I) *with Group VIII*c *Complexes*.—(a) *With dichlorobis*(*diethylphenylphosphine*)*nickel*(II). Upon addition of the olefin (0·25 ml) the red colour of the nickel complex (0·462 g, 1·00 mmol), in acetone (5 ml) containing sodium tetrafluoroborate (0·120 g), became yellow. After stirring for 10 min at 20°, the solvent was removed and the oily residue was washed with dichloromethane (10 ml) and filtered. Addition of ether (15 ml) to the filtrate gave a yellow solid which was twice reprecipitated (CH_2Cl_2–Et_2O and Me_2CO–Et_2O) and identified as trans-*chlorobis*(1,3-*dimethylimidazolidin*-2-*ylidene*)(*diethylphenylphosphine*)*nickel*(II) *tetrafluoroborate* (0·370 g, 70%).

(b) *With dichlorobis*(*triphenylphosphine*)*nickel*(II). The olefin (0·37 ml) was added to a stirred suspension of the nickel complex (0·654 g, 1·00 mmol) in acetone and the colour of the mixture became brown. On heating (40—50°), the precipitate turned to green. The mixture was allowed to cool to 20° and filtered. The filtrate was treated with sodium tetrafluoroborate (0·110 g, 1·00 mmol) at 40—50° for ½ h. The solvent was removed *in vacuo*, the residue was extracted with dichloromethane (15 ml) and addition of ether (15 ml) gave the waxy solid *complex* (XIII) (0·230 g, 49%), analytical date for which (Table 3) show it to be impure.

(c) *With* trans-*dichlorobis*(*triethylphosphine*)*palladium*(II). A solution of the palladium complex (0·413 g, 1·00 mmol) and the olefin (0·25 ml) in toluene (25 ml) was slowly heated to 90—100° and maintained at that temperature for 10 min. A white precipitate deposited. After cooling to 20°, this was filtered off and washed with n-hexane (20 ml). The white solid was dissolved in acetone (20 ml) and was stirred (1 h) with sodium tetrafluoroborate (0·121 g, 1·10 mmol) at 20°. The solvent was removed and the residue was dissolved in dichloromethane (20 ml) and filtered. The volume of the solution was reduced to *ca.* 5 ml and ether (20 ml) was added to obtain trans-*chloro*(1,3-*dimethylimidazolidin*-2-*ylidene*)*bis*(*triethylphosphine*)*palladium*(II) *tetrafluoroborate* (0·490 g, 90%).

(d) *With* trans-*chlorohydridobis*(*triphenylphosphine*)*platinum*(II). When the olefin (0·23 ml) was added to a suspension of the platinum hydride (0·436 g, 0·58 mmol) in toluene (25 ml) the colour of the mixture turned orange-brown. Upon warming to 110°, the colour was discharged. After heating under reflux for 2 h, the mixture was cooled to 20°, and the solid was decanted off and washed with n-hexane (20 ml) to give a hygroscopic solid (i.r. and ^1H n.m.r.). After treatment with sodium tetrafluoroborate (0·110 g, 1·00 mmol), by procedure (c), *hydridotris*(1,3-*dimethylimidazolidin*-2-*ylidene*)*platinum*(II) *tetrafluoroborate* (0·280 g, 80%) was obtained.

A portion of this complex (0·115 g) was dissolved in chloroform (5 ml) and put aside for 24 h. Addition of n-hexane (10 ml) gave a white solid identified as *chlorotris*(1,3-*dimethylimidazolidin*-2-*ylidene*)*platinum*(II) *tetrafluoroborate* (0·110 g, 90%).

(e) *With* cis-*dimethylbis*(*triphenylphosphine*)*platinum*(II). The olefin (0·503 mmol) was added to the platinum complex (0·348 g, 0·503 mmol) in boiling toluene (15 ml) under reflux, and the temperature was so maintained for 35 h. Toluene was removed and diethyl ether (25 ml) was added, which caused the oil to furnish crystals of white cis-*dimethyl*(1,3-*dimethylimidazolidin*-2-*ylidene*)(*triphenylphosphine*)*platinum*(II) (0·208 g, 71%), which was recrystallised ($CHCl_3$–C_6H_{14}).

(f) *With* cis-*dimethylbis*(*dimethylphenylphosphine*)*platinum*(II). Using the procedure of (e), the platinum complex (0·320 g, 0·638 mmol) and olefin (0·63 g, 0·68 mmol) in toluene under reflux (7 h) afforded the white cis-*dimethyl*(1,3-*dimethylimidazolidin*-2-*ylidene*)(*dimethylphenylphosphine*)*platinum*(II) (0·265 g, 90%).

The same product was obtained by increasing by 50% the molar concentration of olefin, and heating under reflux in toluene for 17 h.

(g) *With* cis-*dichlorobis*(*triphenylphosphine*)*platinum*(II). Similarly, in equimolecular proportions, the platinum complex (0·309 g) and olefin (0·225 g) in boiling toluene (3 h), or with a 50% increase in relative proportion of olefin in boiling toluene (5 h), gave hygroscopic cis-*chlorobis*(1,3-*dimethylimidazolidin*-2-*ylidene*)(*dimethylphenylphosphine*)-*platinum*(II) *chloride*, which with aqueous sodium tetrafluoroborate at room temperature yielded the corresponding *tetrafluoroborate*.

(h) *With* cis-*dichlorobis*(*dimethylphenylphosphine*)*platinum*(II). Similarly, using equimolar proportions in toluene under reflux for 1 h, there was obtained a white hygroscopic solid believed to be (XXI) (0·220 g from 0·341 g dichloro-complex), which was converted to the corresponding tetrafluoroborate (XXIII), by treatment with aqueous $NaBF_4$; both (XXI) and (XXII) had i.r. and ^1H n.m.r. characteristics (Table 3) which support the formulations, but analytical data are not available.

(i) *With iodo*(*methyl*)*bis*(*triphenylphosphine*)*platinum*(II). Similarly, using equimolar proportions in toluene under reflux for 2 h, or with a 50% excess of olefin and boiling for 5 h, there was obtained off-white cis-*methylbis*(1,3-*dimethylimidazolidin*-2-*ylidene*)(*triphenylphosphine*)*platinum*(II).

(j) *With* π-*allylbis*(*triphenylphosphine*)*platinum*(II) *chloride*.[29] Using the reagents in equimolar quantities in benzene under reflux for 3 h, there was obtained off-white σ-*allylchloro*(1,3-*dimethylimidazolidin*-2-*ylidene*)(*triphenylphosphine*)*platinum*(II) (67%).

Using a 50% increase in molar equivalent of olefin and heating under reflux for 1·5 h in benzene, gave white σ-*allylbis*(1,3-*dimethylimidazolidin*-2-*ylidene*)(*triphenylphosphine*)*platinum*(II) *chloride* (61%), which with aqueous $NaBF_4$ gave the white corresponding *tetrafluoroborate*.

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[4/226 *Received, 5th February*, 1974]

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[29] H. C. Volger and K. Vrieze, *J. Organometallic Chem.*, 1967, **9**, 527, 537.