Carbene Complexes of Iridium, Rhodium, Manganese, Chromium, and Iron containing Thiazolidinylidene and Pyridinylidene Ligands

By **Paul J. Fraser, Warren R. Roper, and F. Gordon A Stone,*** Department of Inorganic Chemistry, The University, Bristol BS8 1TS

New carbene complexes of Ir^{I}, Rh^{I}, Mn^{I}, Cr^{0}, and Fe^{0} have been prepared by reactions of the appropriate carbonylmetal anions with *N*-methyl- and *N*-ethyl-2-chloro-4-methylthiazolium tetrafluoroborate and *N*-methyl-2-chloropyridinium tetrafluoroborate. The anions $[Ir(CO)_3PPh_3]^-$, $[Rh(CO)_2(PPh_3)_2]^-$, and $[Mn(CO)_5]^-$ afford cationic carbene complexes, whereas $[Cr(CO)_5]^{2-}$ and $[Fe(CO)_4]^{2-}$ yield neutral carbene complexes. Treatment of $[Mn(CO)_5\{\overline{CN(Me)C(Me)CHS}\}][BF_4]$ with iodide ion gives a neutral complex $[cis\text{-}MnI(CO)_4\text{-}\{\overline{CN(Me)C(Me)CHS}\}]$.

The cation $[Ir(CO)\{\overline{CN(Me)C(Me)CHS}\}(PPh_3)_2]^+$ reacts with hydrogen to give $[IrH_2(CO)\{\overline{CN(Me)C(Me)CHS}\}\text{-}(PPh_3)_2]^+$. The cation also reacts oxidatively to give Ir^{III} complexes with HCl, Cl_2, and I_2. Lithium chloride or bromide reacts to give $[IrH(X)(CO)\{\overline{CN(Me)C(Me)CHS}\}(PPh_3)_2][BF_4]$ (X = Cl or Br), whereas $[Ir(CO)\text{-}\{\overline{CN(Me)CHCHCHCH}\}(PPh_3)_2][BF_4]$ affords the neutral Ir^{III} species $[IrCl_3\{\overline{CN(Me)CHCHCHCH}\}(PPh_3)_2]$. Methyl iodide reacts with $[Ir(CO)\{\overline{CN(Me)C(Me)CHS}\}(PPh_3)_2][BF_4]$ to give $[IrI_2Me(CO)\{\overline{CN(Me)C(Me)CHS}\}\text{-}(PPh_3)]$.

Some spectroscopic properties of the new complexes are reported.

SEVERAL routes are available [1-3] for the synthesis of transition metal carbene complexes; one general method involves reactions between electron-rich olefins and complexes with metals in low oxidation states.[4-6] The resulting compounds contain carbene ligands in which the carbene carbon atom is part of a ring system. Similar complexes have been obtained by reactions of carbonylmetal anions with dichloro-1,2-diphenylcyclopropene [7-9] and with 3-ethoxy-1,2-diphenylcyclopropenylium tetrafluoroborate.[10] Heterocyclic carbene complexes can also be formed by hydrogen elimination in reactions of hydridocarbonylmetal anions with cations of the general type (A). Although the resulting complexes do not

---

[1] F. A. Cotton and C. M. Lukehart, *Progr. Inorg. Chem.*, 1972, **16**, 487.

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

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

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

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

[6] D. J. Cardin, B. Cetinkaya, E. Cetinkaya, and M. F. Lappert, *J.C.S. Dalton*, 1973, 514.

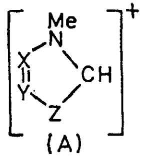
[7] K. Öfele, *Angew. Chem. Internat. Edn.*, 1968, **7**, 950.

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

[9] K. Öfele, *J. Organometallic Chem.*, 1970, **22**, C9.

[10] C. W. Rees and E. von Angerer, *J.C.S. Chem. Comm.*, 1972, 420.

contain heterocyclic carbenes, carbonylmetal anions also react with *N*-chloromethylenedimethylammonium chloride to give carbene complexes.[13]


(A)

X=Y=CH, Z=NMe[7,8,11]
X=Y=CH, Z=S[7,8]
X=Y=N, Z=NMe[7,8,12]
X=N, Y=CH, Z=NMe[7,8]

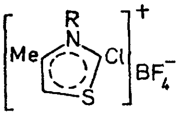
Herein we describe reactions of the borofluoride salts (I)—(III) with several carbonylmetal anions which afford both cationic and neutral cyclic carbene complexes. Some oxidative-addition and substitution reactions of these carbene complexes are also reported. We have previously employed (I) * as a source of transition metal carbene complexes *via* oxidative-addition reactions.[14]

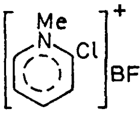
Reaction between the anions $[M(CO)_{4-n}(PPh_3)_n]^-$ (M = Ir, $n = 1$; M = Rh, $n = 2$) and (I) or (II) affords the cationic Ir^I and Rh^I carbene complexes (IV)—(VII). Similarly, treatment of $[Ir(CO)_3(PPh_3)]^-$ with the BF_4^- salt (III) in the presence of an excess of sodium tetraphenylborate yields the tetraphenylborate salt (VIII).

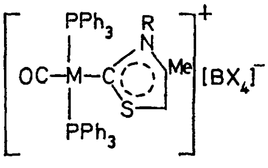
Manganese carbene complexes (IX) and (X) were prepared by reactions of $[Mn(CO)_5]^-$ with (I) and (II), respectively. A number of other cationic Mn^I carbene complexes have recently been characterised.[15] Similarly, by employing the dianion $[Cr(CO)_5]^{2-}$ it has been possible to obtain the Cr^0 complexes (XI) and (XII) from (I) and (II), respectively. The anion $[Fe(CO)_4]^{2-}$ affords with (I) an unstable carbene complex (XIII).

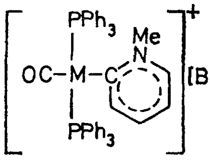
The new complexes were characterised by analysis (Table 1) and by their i.r. and n.m.r. spectra (Table 2). The cationic iridium and rhodium compounds (IV)—(VIII) are yellow air-stable solids with i.r. spectra showing carbonyl stretching bands similar to those of other four-co-ordinate Ir^I and Rh^I cationic species $[M(CO)(L)(PPh_3)_2]^+$ (L = PPh_3, MeCN, Me_2SO, *etc.*).[16,17] These rhodium and iridium complexes are postulated to have a square planar ligand arrangement in which the triphenylphosphine ligands are *trans* to one another. The electron-rich olefin route has also been used to obtain four-co-ordinate Ir^I cationic carbene complexes.[4]

The manganese complexes (IX) and (X) are air-stable solids with i.r. spectra in the carbonyl region


(I) R=Me
(III) R=Et

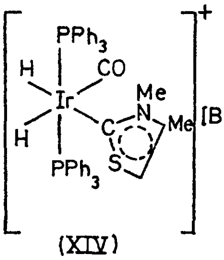

(II)


(IV) M=Ir, R=Me, X=F
(V) M=Rh, R=Me, X=F
(VIII) M=Ir, R=Et, X=Ph


(VI) M=Ir
(VII) M=Rh

$[Mn(CO)_5\{CN(Me)C(Me)CHS\}]^+[BF_4]^-$
(IX)

$[Mn(CO)_5\{CN(Me)CHCHCHCH\}]^+[BF_4]^-$
(X)


(XIV)

$[Cr(CO)_5\{CN(Me)C(Me)CHS\}]$
(XI)

$[Cr(CO)_5\{CN(Me)CHCHCHCH\}]$
(XII)

$[Fe(CO)_4\{CN(Me)C(Me)CHS\}]$
(XIII)

$[IrXH(CO)\{CN(Me)C(Me)CHS\}(PPh_3)_2]^+[BF_4]^-$
(XV) X=Cl (XVI) X=Br

$[IrX_2(CO)\{CN(Me)C(Me)CHS\}(PPh_3)_2]^+[BF_4]^-$
(XVII) X=Cl (XVIII) X=I

$[IrCl_3\{CN(Me)CHCHCHCH\}(PPh_3)_2]$
(XIX)

$[IrI_2(Me)(CO)\{CN(Me)C(Me)CHS\}(PPh_3)]$
(XX)

$[MnI(CO)_4\{CN(Me)C(Me)CHS\}]$
(XXI)

(Table 2) similar to that of the cationic carbene species $[Mn(CO)_5(COCH_2CH_2O)]^+$.[18] The carbonyl i.r. spectra

---

* In reference 14 we incorrectly assigned the structure of the cation used as the *N*-methyl-2-chloro-5-methylthiazolium ion. The ligand in the earlier work was, as in the present study, :CN(Me)C(Me)CHS, derived from 2-chloro-4-methyl-1,3-thiazole. The incorrect positioning of the methyl substituent in ref. 14 makes no difference to the overall chemistry described therein.

[11] K. Öfele, *J. Organometallic Chem.*, 1968, **12**, P42.

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

[13] B. Cetinkaya, M. F. Lappert, and K. Turner, *J.C.S. Chem. Comm.*, 1972, 851.

[14] P. J. Fraser, W. R. Roper, and F. G. A. Stone, *J. Organometallic Chem.*, 1973, **50**, C54; *J.C.S. Dalton*, 1974, 102.

[15] C. H. Game, M. Green, J. R. Moss, and F. G. A. Stone, *J.C.S. Dalton*, 1974, 351.

[16] J. Peone and L. Vaska, *Angew Chem. Internat. Edn.*, 1971, **10**, 511.

[17] C. A. Reed and W. R. Roper, *J.C.S. Dalton*, 1973, 1365.

[18] M. Green, J. R. Moss, I. W. Nowell, and F. G. A. Stone, *J.C.S. Chem. Comm.*, 1972, 1339.

of the neutral Cr^0 complexes (XI) and (XII) are characteristic of those of numerous pentacarbonyl(carbene)chromium compounds.[19]

TABLE 1

Carbene complexes of Ir^I, Ir^{III}, Rh^I, Mn^I, Cr^0, and Fe^0

Complex [a]	M.p. (°C)	Colour	Yield (%)	Analytical data (%) [b] C	H	N
(IV) [c]	230—235 †	Yellow	75	53·0 (53·4)	3·9(3·9)	1·5 (1·5)
(VI) [d]	235—240 †	Yellow	77	52·5 (52·3)	4·1 (3·9)	1·6 (1·4)
(VIII) [e]	247—250 †	Yellow	41	67·6 (67·6)	5·0 (5·0)	1·2 (1·2)
(XIV)	170 †	White	95	53·0 (53·3)	4·3 (4·2)	1·4 (1·5)
(XV)	200—220 †	White	95	51·2 (51·4)	4·0 (3·9)	1·4 (1·4)
(XVI)	190—220 †	White	60	48·9 (49·2)	3·8 (3·7)	1·3 (1·4)
(XVII)	200—220 †	White	90	49·1 (49·6)	3·8 (3·7)	1·4 (1·4)
(XVIII)	196—198	Orange	85	41·9 (42·1)	3·3 (3·1)	1·3 (1·2)
(XIX) [f]	240 †	White	42	54·2 (55·0)	4·2 (4·1)	1·3 (1·5)
(XX) [g]	170—190 †	White	55	34·8 (34·7)	3·1 (2·9)	1·6 (1·6)
(V)	200 †	Yellow	71	60·3 (60·0)	4·4 (4·4)	1·7 (1·6)
(VII) [d]	200 †	Yellow	78	58·0 (57·4)	4·2 (4·3)	1·4 (1·5)
(IX)	140—145	White	71	30·6 (30·4)	1·8 (1·8)	3·5 (3·6)
(X)	130—135	White	75	35·6 (35·2)	1·9 (1·9)	3·7 (3·7)
(XXI)	115—117	Orange	18	26·7 (26·6)	1·8 (1·7)	3·4 (3·4)
(XI)	89—91	Yellow	22	39·9 (39·3)	2·6 (2·3)	4·5 (4·6)
(XII)	79—80	Yellow	45	46·3 (46·3)	2·5 (2·5)	5·0 (4·9)
(XIII)	60—70	Red	53	38·0 (38·4)	2·6 (2·5)	4·5 (5·0)

† Decomp.

[a] L = PPh_3. [b] Calc. values in parentheses. [c] Molar conductance in nitrobenzene (Ω^{-1} cm^{-1}) 27·1 ($1·00 \times 10^{-3}$M). [d] CH_2Cl_2 solvate (1:1). [e] Molar conductance in nitrobenzene (Ω^{-1} cm^{-1}) 14·4 ($0·67 \times 10^{-1}$M). [f] Molar conductance in nitrobenzene (Ω^{-1} cm^{-1}) < 0·2 ($1·00 \times 10^{-3}$M). [g] Molar conductance in nitrobenzene (Ω^{-1} cm^{-1}) < 0·2 ($1·20 \times 10^{-3}$M).

The i.r. spectrum of $[Fe(CO)_4\{\overline{CN(Me)C(Me)CHS}\}]$ (XIII) shows three bands in the carbonyl stretching region, as expected for a molecule of C_{3v} symmetry containing the carbene ligand in the axial position. Complex (XIII) is a red-brown, very air-sensitive, solid. It can, however, be handled under nitrogen in tetrahydrofuran solution without appreciable decomposition. Stabilisation of the complex in tetrahydrofuran might be a result of Lewis acid–base complexation of the cyclic ether with the carbene carbon atom.[20] A similar complexation has been observed with $[Cr(CO)_5\{C(OMe)Ph\}]$ and dimethylphosphine.[21]

Compounds (I) and (III) show characteristic i.r. bands at 1588 and 1585 cm^{-1}, respectively. Bands near these frequencies are observed in the spectra of all complexes (Table 2) containing the *N*-alkylthiazolidinylidene ligands $:\overline{CN(R)C(Me)CHS}$ (R = Me or Et) and are tentatively assigned to the C:C stretching frequency.

TABLE 2

I.r.[a] and ^1H n.m.r. data for the complexes

Compound [b]	ν_{CO}/cm^{-1}	$\nu_{C:C}/cm^{-1}$	Chemical shift (τ) [c]
(I)		1588	[d] C*Me*, 7·43d ($^4J_{HH}$ 1 Hz); N*Me* 6·03; C*H* 2·22q
(II)			[d] N*Me* 5·73s; C_5H_4N 1·70m
(III)		1585	[e] CH_2*Me* 8·47t ($^3J_{HH}$ 7·3 Hz); C*Me* 7·30s; CH_2Me 5·36q; C*H* 2·07s
(IV)	1993	1585	C*Me* 8·20s; N*Me* 7·28s; C*H* 2·90s; P*Ph* 2·50m
(VI)	1985		N*Me* 6·57s; C_5H_4N, P*Ph*, 2·52m
(VIII)	1984	1580	[f] CH_2*Me*, 9·24t 8·92t, ($^3J_{HH}$ 7·5 Hz); C*Me*, 7·93s; CH_2Me, 6·37m; C*H*, 3·22s; P*Ph*, B*Ph*, 2·50m
(XIV)	2011 2135 [g] 2057 [g]	1582	C*Me*, 7·97s; N*Me*, 7·18s; C*H*, 2·73s; P*Ph*, 2·55m; Ir*H*, 22·69t of d; 19·53t of d ($^2J_{PH}$ 16·5; $^2J_{HH}$ 4·5 Hz)
(XV)	2050 2251 [g]	1586	C*Me*, 7·92s; N*Me*, 6·88s; C*H*, 3·09s; P*Ph*, 2·57m; Ir*H*, 25·5t ($^2J_{PH}$ 12 Hz)
(XVI)	2063 2279 [g]	1584	C*Me*, 7·95s; N*Me*, 6·87s; C*H*, 3·18s; P*P*h, 2·60m; Ir*H*, 24·59t ($^2J_{PH}$ 12 Hz)
(XVII)	2081	1588	
(XVIII)	2058	1578	
(XX)	2014	1589	Ir*Me*, 8·80d ($^3J_{PH}$ 5 Hz); C*Me*, 7·54s; N*Me*, 5·70s; C*H*, 2·80s; P*P*h, 2·62m, 1·98m
(XIX)			N*Me*, 6·08s; C_5H_4N, P*Ph*, 2·75m
(V)	2006	1583	C*Me*, 8·15s; N*Me*, 7·13s; C*H*, 2·98s; P*Ph*, 2·57m
(VII)	2001		N*M*e, 6·48s; C_5H_4N, P*P*h, 2·57m
(IX)	2143m 2090m 2052vs	1590	C*Me*, 7·50s; N*Me*, 5·95s; C*H*, 3·43s
(X)	2138m 2078m 2032vs		[f] N*Me*, 5·57s; C_5H_4N, 2·37m, 1·72m, 1·33m (2 : 1 : 1)
(XXI)	2080m 2000s 1978vs 1946s	1585	C*Me*, 7·45s; N*Me*, 5·78s: C*H*, 2·78s
(XI)	2055m 1969m 1925vs	1583	C*Me*, 7·58s; N*Me*, 6·33s; C*H*, 3·10s
(XII)	2046m 1954w 1914vs		N*Me*, 5·60s; C_5H_4N, 2·98m, 1·95m, 1·63m (2 : 1 : 1)
(XIII)	2040m 1955m 1925vs	1588	C*Me*, 7·57s; N*Me*, 5·93s; C*H*, 2·97s

[a] Nujol, except for (IX)—(XI) and (XXI) measured in CH_2Cl_2, and (XIII) in $[CH_2]_4O$. [b] L = PPh_3. [c] Measured in $CDCl_3$ unless otherwise stated. [d] Measured in CD_3CN. [e] Measured in $(CD_3)_2CO$. [f] Measured in CD_3CN. [g] ν_{IrH}.

It was possible to record the mass spectra of the neutral carbene complexes (XI)—(XIII). The breakdown patterns found are similar to those observed in the spectra of other cyclic and non-cyclic carbene complexes of Cr^0 and Fe^0.[10,22-24] Ions $[M\{\overline{CN(Me)C(Me)CHS}\}]^+$ (M = Cr or Fe) observed in the spectra of (XI) and (XIII) release C_3H_4 (MeC:CH?), forming fragments corresponding to $[\overline{MCN(Me)S}]^+$; these three-membered cyclic carbene systems undergo loss of MeNC. A related mode of decomposition has been observed in the mass spectra of $[M\{\overline{CN(Me)X{:}YN(Me)}\}]^+$ (M = Cr or Fe, X:Y = CH:CH, N:CH, or N:N).[24] No ions were found in the spectra of (XI)—(XIII) corresponding to the free carbene or its dimerisation product. The formation of olefins as a product of the thermal decomposition of carbene–chromium complexes in the mass spectrometer has been shown to be critically dependent on the nature of the heteroatom substituents of the carbene ligand.[25]

The co-ordinatively unsaturated Ir^I carbene complex

---

[19] E. O. Fischer, *Pure Appl. Chem.*, 1970, **24**, 407; and references cited therein.

[20] G. M. Bodner, S. B. Kahl, K. Bork, B. N. Storhoff, J. E. Wuller, and L. J. Todd, *Inorg. Chem.*, 1973, **12**, 1071.

[21] F. R. Kriessl, C. G. Kreiter, and E. O. Fischer, *Angew. Chem. Internat. Edn.*, 1972, **11**, 643.

[22] J. Muller and J. A. Connor, *Chem. Ber.*, 1969, **102**, 1148.

[23] E. O. Fischer, H. J. Beck, C. G. Kreiter, J. Lynch, J. Muller, and E. Winkler, *Chem. Ber.*, 1972, **105**, 162.

[24] J. Muller, *Angew Chem. Internat. Edn.*, 1972, **11**, 653.

[25] J. A. Connor and E. M. Jones, *J. Organometallic Chem.*, 1971, **31**, 389.

(IV) readily undergoes oxidative-addition reactions with hydrogen, hydrogen chloride, and chlorine or iodine to afford the cationic Ir^{III} complexes (XIV), (XV), (XVII), and (XVIII). The carbonyl stretching bands in the i.r. of the cations (XV)—(XVIII) (Table 2) are in the range (2050—2081 cm^{-1}) typical of Ir^{III} cationic carbonyl carbene complexes.[14]

The ^{1}H n.m.r. spectrum of (XIV) (Table 2) shows two metal hydride signals at τ 19·53 and 22·69, occurring as triplets of doublets ($^2J_{PH}$ 16·5; $^2J_{HH}$ 4·5 Hz) indicating the presence of two magnetically equivalent phosphine ligands with each hydride ligand *cis* to both phosphine ligands, and with a small coupling between the two protons. Structure (XIV) is further supported by the observation in the i.r. of two Ir–H stretching frequencies. Similar *trans*-phosphine *cis*-hydride structures have been proposed for $[IrH_2Cl(CO)(PPh_3)_2]$,[26] $[IrH_2Cl(CO)(PMe_2Ph)_2]$,[27] and $[IrH_2(CO)(CS)\{P(cyclohexyl)_3\}_2]^+$.[28] The lower ν_{IrH} in the spectrum of (XIV) probably corresponds to the H ligand *trans* to the carbene ligand, with the higher ν_{IrH} frequency arising from the H ligand *trans* to CO, since carbene ligands have been shown to be comparable with phosphines in their σ-donor character.[29]

The ^{1}H n.m.r. spectra of (XV) and (XVI) show triplet signals at τ 25·50 and 24·59, respectively, as expected if the hydride ligand in each complex is *cis* to two magnetically equivalent *trans*-phosphine ligands, and possibly *trans* to halide. Hydrido-ligands *trans* to halides resonate at high field and exhibit high values for ν_{IrH}.[26,27] This stereochemistry would result from *trans*-addition of hydrogen halide in (XV) and (XVI).

Attempts to prepare neutral Ir^I carbene complexes from reactions between (IV) and anionic ligands proved unsuccessful. However, prolonged treatment of (IV) with lithium chloride in ethanol yielded (XV). Lithium bromide behaved in the same way to give (XVI). Interestingly, prolonged treatment of the *N*-methylpyridinylidene complex (VI) with lithium chloride in methanol gave the neutral Ir^{III} species (XIX). No reaction was observed between (IV) and lithium chloride in C_6F_6 as solvent, or with tetra-alkylammonium halides in methanol, or with sodium methoxide in methanol. Prolonged treatment of (IV) with $NaBH_4$ in methanol gave (XIV), presumably *via in situ* formation of hydrogen. Treatment of (V) with an excess of tetraethylammonium iodide in methanol gave $[RhI(CO)(PPh_3)_2]$. The fate of the displaced carbene was not established.

When (IV) was treated with an excess of methyl iodide, the Ir^{III} species (XX) was obtained. Molar conductance studies on (XX) and (XIX) (Table 1) showed that the complexes were neutral species. Presumably (XX) is formed by reaction of the expected $[IrI(Me)(CO)\{\overline{CN(Me)C(Me)CHS}\}(PPh_3)_2][BF_4]$ with methyl iodide, leading to loss of one molecule of triphenylphosphine, perhaps as $[PPh_3Me]BF_4$.

Treatment of the dihydro-complex (XIV) with an excess of lithium chloride in methanol gave (XV). Whether (XV) arises in this reaction *via* halide attack on (XIV), or hydrogen chloride attack on (IV), formed *in situ* by reversible loss of hydrogen from (XIV), is not certain.

No reaction was observed when (XIV) was treated with an excess of triphenylphosphine.

The cationic manganese carbene complex (IX) reacts with tetraethylammonium iodide to give neutral $[cis\text{-}MnI(CO)_4\{\overline{CN(Me)C(Me)CHS}\}]$ (XXI). This method has been used to prepare other neutral carbene manganese complexes.[15,18] The i.r. spectrum (Table 2) shows four carbonyl stretching frequencies (3A′ + A″) indicative of a *cis*-disubstituted octahedral complex with C_s symmetry. The mass spectrum of (XXI) showed a fragmentation pattern corresponding to the breakdown of the parent ion as well as the *in situ* formation of the binuclear complex $[Mn_2I_2(CO)_8]$.[30] In contrast to the mass spectra of (XI)—(XIII), the spectrum of (XXI) showed a strong peak corresponding to the free carbene ligand. It has been shown that $[MnI(CO)_5]$ and $[Mn_2I_2(CO)_8]$ are products of the thermal decomposition of the carbene complex $[cis\text{-}MnI(CO)_4(\overline{COCH_2CH_2CH_2})]$.[15]

EXPERIMENTAL

^{1}H N.m.r. spectra were recorded on Varian T60 and HA100 spectrometers. I.r. spectra were measured with a Perkin-Elmer 457 spectrophotometer, and mass spectra with an A.E.I. MS902 spectrometer operating at 70 eV ionisation potential. Conductivity measurements were recorded with a Cambridge conductance bridge, using platinum electrodes. Solvents were dried and distilled under nitrogen before use and all reactions were carried out under oxygen-free nitrogen.

The anions $[Ir(CO)_3PPh_3]^-$ and $[Rh(CO)_2(PPh_3)_2]^-$ were prepared as described elsewhere.[31] Other anions were prepared by standard procedures except that $[Mn(CO)_5]^-$ was isolated before use by employing the counter-ion $[(Ph_3P)_2N]^+$.[32]

2-*Chloro*-3,4-*dimethylthiazolium tetrafluoroborate* (I), m.p. 203—205°, was obtained (95%) (Found: C, 25·7; H, 3·0; N, 6·0. $C_5H_7BClF_4NS$ requires C, 25·5; H, 3·0; N, 5·9%) by treating 2-chloro-4-methylthiazole with $[Me_3O][BF_4]$ in dichloromethane–acetonitrile (3 : 1). 2-*Chloro*-1-*methylpyridinium tetrafluoroborate* (II), m.p. 148—149°, was prepared (95%) (Found: C, 33·8; H, 2·8; N, 6·6. $C_6H_7BClF_4N$ requires C, 33·5; H, 3·5; N, 6·5%) by treating 2-chloropyridine with $[Me_3O][BF_4]$ in dichloromethane–acetonitrile (3 : 1). 2-*Chloro*-3-*ethyl*-4-*methylthiazolium tetrafluoroborate* (III), m.p. 190—195°, was obtained (90%) (Found: C, 28·1; H, 3·6; N, 5·5. $C_6H_9BClF_4NS$ requires

---

[26] R. C. Taylor, J. F. Young, and G. Wilkinson, *Inorg. Chem.*, 1966, **5**, 20.

[27] A. J. Deeming and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 1128.

[28] M. J. Mays and F. P. Stefanini, *J. Chem. Soc.* (*A*), 1971, 2747.

[29] M. Y. Darensbourg and D. J. Darensbourg, *Inorg. Chem.*, 1970, **9**, 32.

[30] K. Edgar, B. F. G. Johnson, J. Lewis, I. G. Williams, and J. M. Wilson, *J. Chem. Soc.* (*A*), 1967, 379.

[31] J. P. Collman, F. D. Vastine, and W. R. Roper, *J. Amer. Chem. Soc.*, 1968, **90**, 2282.

[32] J. K. Ruff, *Inorg. Chem.*, 1968, **7**, 1818.

C, 28·9; H, 3·6; H, 5·6%) by treating 2-chloro-4-methylthiazole with $[Et_3O][BF_4]$ in dichloromethane–acetonitrile (3 : 1).

Synthesis of the Carbene Complexes.—(*a*) $[Ir(CO)\{\overline{CN(Me)C(Me)CHS}\}(PPh_3)_2]BF_4$ (IV) was prepared by treating $[Ir(CO)_3PPh_3]^-$ (1·0 mmol) in tetrahydrofuran (25 ml) with (I) (1·0 mmol) for 0·5 h. The yellow *precipitate* was crystallised from dichloromethane by slow addition of cyclohexane.

Complex (VI), obtained in the same manner from (II), was isolated by slow addition of diethyl ether to a solution in dichloromethane.

Similarly (VIII) was obtained as an oil, which was taken up in dichloromethane; cyclohexane was slowly added in the presence of $NaBPh_4$ to afford *crystals.*

(*b*) $[Rh(CO)\{\overline{CN(Me)C(Me)CHS}\}(PPh_3)_2][BF_4]$ (V) was prepared by reaction of $[Rh(CO)_2(PPh_3)_2]^-$ (1·0 mmol) in tetrahydrofuran (25 ml) with (I) (1·0 mmol) for ½ h. The yellow precipitate gave *crystals* of (V) from dichloromethane to which hexane was slowly added.

Complex (VII), similarly obtained from (II), gave *crystals* from dichloromethane–diethyl ether.

(*c*) $[Mn(CO)_5\{\overline{CN(Me)C(Me)CHS}\}][BF_4]$ (IX) was synthesised by reaction of $[(Ph_3P)_2N][Mn(CO)_5]$ (1·36 mmol) in dichloromethane (5 ml) with (I) (1·36 mmol) for 15 min. White *crystals* were obtained by careful addition of diethyl ether until the solution became cloudy, followed by cooling to 0°. *Complex* (X) was obtained from (II) and $[(Ph_3P)_2N][Mn(CO)_5]$ in a similar manner.

(*d*) $[Cr(CO)_5\{\overline{CN(Me)C(Me)CHS}\}]$ (XI) was obtained by reaction of $Na_2[Cr(CO)_5]$ (5·0 mmol) in tetrahydrofuran (30 ml) at $-20°$ with (I) (4·5 mmol), added over 1 h. The solution was warmed to room temperature, concentrated (10 ml), and chromatographed on silica gel with diethyl ether as eluant. The yellow product was sublimed (80° and 0·15 Torr), some $Cr(CO)_6$ subliming first, and yellow *crystals* of (XI) were obtained from hot hexane.

Complex (XII) was prepared similarly from (II) as yellow *crystals* from hot hexane.

(*e*) $[Fe(CO)_4\{\overline{CN(Me)C(Me)CHS}\}]$ (XIII) was prepared by treating $Na_2[Fe(CO)_4]$ (5·00 mmol) in tetrahydrofuran (20 ml) at $-20°$ with (I) (4·50 mmol), added over 1 h. After warming to room temperature and concentrating (to 10 ml), the solution was chromatographed on silica gel, with tetrahydrofuran as eluant. The orange-red eluate was evaporated to a red-brown *solid.*

Reactions of the Carbene Complexes.—$[Ir(CO)\{\overline{CN(Me)C(Me)CHS}\}(PPh_3)_2]BF_4$ (IV). (i) *Hydrogen.* Complex (XIV) was prepared by bubbling hydrogen through a solution (10 ml) of (IV) (1·0 mmol) in dichloromethane for 12 h. White *crystals* were isolated on addition of hexane. Compound (XIV) was also obtained (65% yield) on treatment of (IV) (0·5 mmol) with an excess of $NaBH_4$ in methanol (15 ml) for 8 h.

(ii) *Hydrogen chloride.* Compound (XV) was prepared by passing hydrogen chloride through a sample (0·25 mmol) of (IV) in dichloromethane (5 ml). Addition of hexane gave *crystals* (from dichloromethane–hexane). The same product (XV) was also obtained (71% yield) when (IV) (0·25 mmol) was refluxed in ethanol (15 ml) for 16 h with a slight excess of lithium chloride.

(iii) *Lithium bromide.* Complex (XVI) was prepared by refluxing (IV) (0·25 mmol) with a slight excess of lithium bromide in ethanol (15 ml) for 16 h. *Crystals* were obtained from dichloromethane–cyclohexane.

(iv) *Chlorine.* Complex (XVII) was prepared by passing chlorine gas through a solution (5 ml) of (IV) (0·25 mmol) in dichloromethane. Addition of hexane gave a white solid, and *crystals* were obtained from dichloromethane–cyclohexane.

(v) *Iodine.* Complex (XVIII) was prepared by addition of iodine (0·25 mmol) in dichloromethane (1 ml) to a solution of (IV) (0·25 mmol) in the same solvent (5 ml). After 15 min light petroleum was added to the orange solution affording a yellow solid which gave *crystals* from dichloromethane–hexane.

(vi) *Methyl iodide.* Compound (XX) was prepared by refluxing a sample of (IV) (0·50 mmol) in methyl iodide (2 ml) for 16 h. *Crystals* were obtained from dichloromethane–cyclohexane.

Reaction of $[Ir(CO)\{\overline{CN(Me)CHCHCHCH}\}(PPh_3)_2][BF_4]$ (VI) *with Lithium Chloride.*—Complex (XIX) was prepared by refluxing (VI) (0·5 mmol) and an excess of lithium chloride in methanol (20 ml) for 72 h. The precipitate gave *crystals* of (XIX) from dichloromethane–hexane.

Reaction of $[Rh(CO)\{\overline{CN(Me)C(Me)CHS}\}(PPh_3)_2][BF_4]$ (V) *with Tetraethylammonium Iodide.*—Treatment of (V) (0·5 mmol) with an excess of Et_4NI in methanol (reflux) for 24 h gave a yellow precipitate, recrystallised from dichloromethane–hexane and identified by i.r. spectroscopy as $[RhI(CO)(PPh_3)_2]$ (0·12 mmol, 24%), ν_{CO} 1983 cm^{-1} (lit.,[33] 1981 cm^{-1}).

Reaction of $[Mn(CO)_5\{\overline{CN(Me)C(Me)CHS}\}][BF_4]$ (IX) *with Tetraethylammonium Iodide.*—A sample of (IX) (1·00 mmol) with an excess of Et_4NI was refluxed in methanol (15 ml) for 46 h. The resulting orange solution was evaporated to dryness and the residue washed with water (2 × 10 ml). The resulting oil was dissolved in dichloromethane (10 ml) and the solution filtered. Hexane was added slowly until the solution became cloudy. On storage at 0° crystals of Et_4NI were deposited. The orange filtrate was reduced in volume and chromatographed on Florisil with diethyl ether as eluant. An orange band was eluted; evaporation of the eluate gave *crystals* of (XXI) (from diethyl ether–cyclohexane).

Mass Spectra.—*Complex* (XI). *m/e* 305 (16·5%, *M*), 277 (2·9, $M - CO$), 249 (<1, $M - 2CO$), 221 (5·4, $M - 3CO$), 193 (23·4, $M - 4CO$), 165 (100·0, $M - 5CO$), 150 (3·2, $M - 5CO - Me$), 125 (3·9. $M - 5CO - C_3H_4$), 84 (4·7, $M - 5CO - C_5H_7N$), and 52 (23·8, $M - 5CO - C_5H_7NS$).

Complex (XII). *m/e* 285 (20·5%, *M*), 257 (4·7, $M - CO$), 229 (1·4, $M - 2CO$), 201 (6·1, $M - 3CO$), 273 (28·6, $M - 4CO$), 245 (100·0, $M - 5CO$), 230 (28·6, $M - 5CO - Me$), 79 (20·0, $M - 5CO - C_5H_6$), and 52 (52·1, $M - 5CO - C_6H_7N$).

Complex (XIII). *m/e* 281 (9·4%, *M*), 253 (20·6, $M - CO$), 225 (6·2, $M - 2CO$), 197 (41·3, $M - 3CO$), 169 (100, $M - 4CO$), 154 (4·7, $M - 4CO - Me$), 129 (22·1, $M - 4CO - C_3H_4$), 88 (8·7, $M - 4CO - C_5H_7N$), and 56 (17·4, $M - 4CO - C_5H_7NS$).

We thank the S.R.C. for support and the University of Auckland for study leave (to W. R. R.).

[3/1686 *Received, 8th August,* 1973]

---

[33] J. P. Collman, M. Kubota, F. D. Vastine, J. Y. Sun, and J. W. Kang, *J. Amer. Chem. Soc.*, 1968, **90**, 5430.