Cationic Cyclic Carbene Complexes of Iridium(III), Nickel(II), Palladium(II), and Platinum(II)

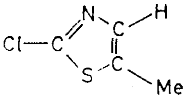
By **Paul J. Fraser, Warren R. Roper,** and **F. Gordon A. Stone,*** Department of Inorganic Chemistry, The University, Bristol BS8 1TS

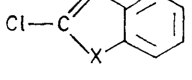
Reaction of the 2-chloro-derivatives of 5-methyl-1,3-thiazole, benzthiazole, and benzoxazole with IrCl(CO)(PMe$_2$Ph)$_2$ affords Ir$^{\mathrm{III}}$ complexes which on protonation yield cationic carbene complexes [IrCl$_2$(CO)(PMe$_2$Ph)$_2$(L)]$^+$ (L = CNHCHC(Me)S, CNHC$_6$H$_4$S, CNHC$_6$H$_4$O). Treatment of IrCl(CO)(PMe$_2$Ph)$_2$ with the *N*-methyl salt of 2-chloro-5-methyl-1,3-thiazole, [ClCN(Me)CHC(Me)S][BF$_4$], affords the carbene complex [IrCl$_2$(CO)(PMe$_2$Ph)$_2${CN(Me)CHC(Me)S}][BF$_4$]. Similar oxidative-addition of [ClCN(Me)CHC(Me)S][BF$_4$] to Pt(PEt$_3$)$_2$(stilbene), Pt(PMePh$_2$)$_4$, PdL$_4$ (L = PPh$_3$, PMePh$_2$) or Ni(PPh$_3$)$_4$ gives cationic carbene complexes of Pt$^{\mathrm{II}}$, Pd$^{\mathrm{II}}$, and Ni$^{\mathrm{II}}$. The complex [PtCl{CNHCHC(Me)S}(PEt$_3$)$_2$][BF$_4$] was obtained by treating PtCl(C:NCH:C(Me)S)(PEt$_3$)$_2$ with fluoroboric acid. Some chemical and spectroscopic properties of the new complexes are discussed.

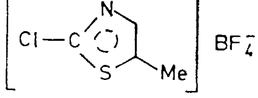
ALTHOUGH not recognised as such, the first cationic carbene complexes of platinum(II) were isolated some fifty years ago.[1,2] Spectroscopic and *X*-ray single crystal structural investigations [3,4] have established the nature of these compounds. Recent reviews [5,6] summarise the available synthetic routes to carbene–metal complexes. A general synthesis which can afford both neutral and cationic carbene complexes has evolved from the use of electron-rich olefins such as 1,1′-dimethyl-2,2′-bibenzothiazolinylidene and 1,1′,3,3′-tetramethyl-2,2′-bi-imidazolidinylidene.[7-9]

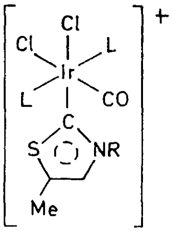
We report herein a simple oxidative-addition route to cationic cyclic-carbene complexes of Ir$^{\mathrm{III}}$, Ni$^{\mathrm{II}}$, Pd$^{\mathrm{II}}$, and Pt$^{\mathrm{II}}$ based on either: (i) reactions of the 2-chloro-derivatives of 5-methylthiazole (I), benzthiazole, or benzoxazole (II) with d^8 or d^{10} complexes followed by protonation at nitrogen; or (ii) reactions of the borofluoride salt of *N*-methyl-2-chloro-5-methylthiazole (III) with d^8 or d^{10} complexes.[10] The first cationic Ir$^{\mathrm{III}}$ carbene complexes have only recently been reported,[11] being formed from reactions of cationic Ir$^{\mathrm{III}}$ compounds with terminal hydroxyacetylenes in methanol. The ability of transition metal complexes containing the $\mathrm{M{-}\overset{\diagdown}{C}{=}NR}$ group to be protonated readily has been used previously as a route to carbene or carbon-bonded ylide complexes of rhodium [12] and iron.[13]

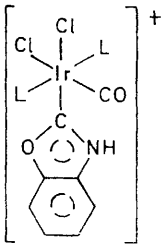
The Ir$^{\mathrm{I}}$ complex IrCl(CO)(PMe$_2$Ph)$_2$ [14] reacts with an excess of compounds (I—II) to afford the neutral Ir$^{\mathrm{III}}$ σ-complexes IrCl$_2$(CO)(C:NCH:C(Me)S)(PMe$_2$Ph)$_2$ (IV), IrCl$_2$(CO)(C:NC$_6$H$_4$O)(PMe$_2$Ph)$_2$ (V) and IrCl$_2$(CO)(C:NC$_6$H$_4$S)(PMe$_2$Ph)$_2$ (VI), respectively. Although (IV)

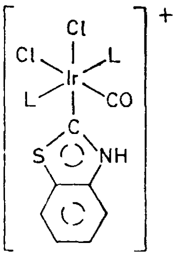

(I)


(IIa, X = S)
(IIb, X = O)


(III)


(VII) R = H
(X) R = Me


(VIII)


(IX)

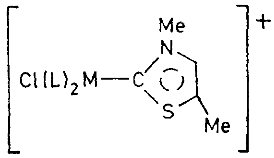

(XII) M = Pt; L = PEt$_3$
(XIII) M = Pt; L = PMePh$_2$
(XIV) M = Pd; L = PPh$_3$
(XV) M = Pd; L = PMePh$_2$
(XVI) M = Ni; L = PPh$_3$

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TABLE 1

Analytical [a] and physical data for the complexes

	Compound	M.p. (t/°C)	Colour	Yield (%)	C	H	N
(V)	$\mathrm{IrCl_2(CO)(C{:}NC_6H_4O)L_2}$ [b]	232—233	White	38	41·8(42·1)	4·0(3·8)	2·2(2·0)
(VI)	$\mathrm{IrCl_2(CO)(C{:}NC_6H_4S)L_2}$ [c]	230—231	White	49	40·9(41·1)	3·8(3·7)	2·0(2·0)
(VII) [d]	$\mathrm{[IrCl_2(CO)(CHNCHC(Me)S)L_2]^+}$ [e]	243—245	White	71	33·5(33·5)	3·6(3·6)	1·9(1·9)
(XI) [f]	$\mathrm{[IrCl_2(CO)(CNHCHC(Me)S)L_2]^+}$	dec. *ca.* 250	White	75	31·8(31·8)	3·4(3·4)	1·9(1·8)
(VIII) [d]	$\mathrm{[IrCl_2(CO)(CNHC_6H_4O)L_2]^+}$	271—273	White	62	37·5(37·3)	3·7(3·5)	2·0(1·8)
(VIII) [g]	$\mathrm{[IrCl_2(CO)(CNHC_6H_4O)L_2]^+}$	279—280	White	81	37·0(36·7)	3·2(3·5)	
(IX) [d]	$\mathrm{[IrCl_2(CO)(CNHC_6H_4S)L_2]^+}$ [h]	250—253	White	47	36·5(36·5)	3·2(3·4)	1·8(1·8)
(IX) [g]	$\mathrm{[IrCl_2(CO)(CNHC_6H_4S)L_2]^+}$ [i]	259—260	White	73	35·9(35·9)	3·3(3·4)	1·8(1·7)
(X) [d]	$\mathrm{[IrCl_2(CO)(CN(Me)CHC(Me)S)L_2]^+}$	269—271	White	70	34·3(34·4)	3·9(3·8)	1·9(1·8)
(XII) [d]	$\mathrm{[PtCl(CN(Me)CHC(Me)S)(PEt_3)_2]^+}$	209—211	White	90	30·5(30·6)	5·4(5·6)	2·4(2·1)
(XIII) [d]	$\mathrm{[PtCl(CN(Me)CHC(Me)S)(PMePh_2)_2]^+}$	220—222	White	89	44·7(44·8)	4·0(4·0)	2·0(1·7)
(XIV) [d]	$\mathrm{[PdCl(CN(Me)CHC(Me)S)(PPh_3)_2]^+}$	dec. *ca.* 230	White	81	56·6(56·8)	4·2(4·3)	1·7(1·6)
(XV) [d]	$\mathrm{[PdCl(CN(Me)CHC(Me)S)(PMePh_2)_2]^+}$	dec. 135	White	70	49·4(50·0)	4·4(4·5)	2·0(1·9)
(XVI) [d]	$\mathrm{[NiCl(CN(Me)CHC(Me)S)(PPh_3)_2]^+}$	dec. *ca.* 160	Yellow	85	59·6(60·1)	4·5(4·6)	1·7(1·7)
(XVII) [d]	$\mathrm{[PdI(CN(Me)CHC(Me)S)(PPh_3)_2]^+}$	dec. *ca.* 200	Yellow	65	50·9(51·4)	3·9(3·9)	1·4(1·5)
(XVIII)	$\mathrm{PtCl(C{:}NCH{:}C(Me)S)(PEt_3)_2}$	84—86	White	84	34·3(34·0)	5·9(6·1)	2·7(2·5)
(XIX) [d]	$\mathrm{[PtCl(CNHCHC(Me)S)(PEt_3)_2]^+}$	178—179	White	55	29·4(29·4)	5·4(5·4)	2·1(2·2)

[a] Calculated values given in parentheses. [b] L = $\mathrm{PMe_2Ph}$. [c] Found: Cl, 10·2. Reqd.: 10·1%. [d] $\mathrm{BF_4^-}$ Salt. [e] Found: Cl, 9·5. Reqd.: 9·4%. [f] $\mathrm{I^-}$ Salt. [g] $\mathrm{ClO_4^-}$ Salt. [h] Found: Cl, 8·8. Reqd.: 9·0%. [i] Found: Cl, 13·1. Reqd.: 13·3%.

TABLE 2

I.r. ($\mathrm{cm^{-1}}$) [a] and ^{1}H n.m.r. (τ) data for the iridium complexes

	Complex [b]	ν(CO)	ν(NH)	Chemical shifts
(IV)	$\mathrm{IrCl_2(CO)(C{:}NCH{:}C(Me)S)L_2}$	2050		[c] P*Me*, 8·33 (t), 7·93 (t); [d] C*Me*, 7·73 (s); C*H*, 3·48 (s); P*Ph*, 2·57 (m)
(VII)	$\mathrm{[IrCl_2(CO)(CNHCHC(Me)S)L_2]BF_4}$	2078	3240, 3200	[e] P*Me*, 8·05 (t), 7·82 (t); [d] C*Me*, 7·89 (s); C*H*, 3·15 (s); *PPh*, 2·60 (m)
(XI)	$\mathrm{[IrCl_2(CO)(CNHCHC(Me)S)L_2]I}$	2075	3350	[c] P*Me*, 7·92 (t), 7·55 (t); [d] C*Me*, 7·60 (s); C*H*, 3·70 (s); P*Ph*, 2·70 (m)
(V)	$\mathrm{[IrCl_2(CO)(C{:}NC_6H_4O)L_2}$	2071		[c] P*Me*, 8·25 (t), 7·87 (t); [d] P*Ph*, and C_6H_4, 2·67 (m)
(VIII)	$\mathrm{[IrCl_2(CO)(CNHC_6H_4O)L_2]BF_4}$	2085	3282, 3240	[e] P*Me*, 7·95 (t), 7·75 (t); [d] P*Ph* and C_6H_4, 2·83 (m), 2·63 (m)
	$\mathrm{[IrCl_2(CO)(CNHC_6H_4O)L_2]ClO_4}$	2089	3250	[e] P*Me*, 8·01 (t), 7·80 (t); [d] P*Ph* and C_6H_4, 2·69 (m)
(VI)	$\mathrm{[IrCl_2(CO)(C{:}NC_6H_4S)L_2}$	2069		[c] P*Me*, 8·30 (t), 7·89 (t); [d] P*Ph* and C_6H_4, 2·67 (m)
(IX)	$\mathrm{[IrCl_2(CO)(CNHC_6H_4S)L_2]BF_4}$	2071	3200, 3100	[e] P*Me*, 8·05 (t), 7·81 (t); [d] P*Ph* and C_6H_4, 2·54 (m)
	$\mathrm{[IrCl_2(CO)(CNHC_6H_4S)L_2]ClO_4}$	2072	3140	[e] P*Me*, 7·97 (t), 7·75 (t); [d] P*Ph* and C_6H_4, 2·70 (m)
(X)	$\mathrm{[IrCl_2(CO)(CN(Me)CHC(Me)S)L_2]BF_4}$	2071		[e] P*Me*, 8·12 (t), 7·67 (t); [d] C*Me*, 7·67 (s); N*Me*, 6·72 (s); C*H*, 3·00 (s); P*Ph*, 2·63 (m)

[a] Nujol mull. [b] L = $\mathrm{PMe_2Ph}$. [c] Measured in $\mathrm{CDCl_3}$. [d] $|^2J(\mathrm{PH}) + {}^4J(\mathrm{PH})|$ 9 Hz. [e] Measured in $\mathrm{CD_3CN}$.

was not isolable analytically pure, protonation of all three compounds with $HClO_4$ or HBF_4 gives the crystalline cationic complexes (VII)—(IX) ($L = PMe_2Ph$).

These protonation reactions are reversible and base converts the cations to the neutral Ir^{III} σ-complexes: *e.g.* (VI) $\underset{HO^-}{\overset{H^+}{\rightleftharpoons}}$ (IX). In contrast to protonation, alkylation of the neutral complexes (IV)—(VI) by trialkyloxonium salts was not successful, perhaps for steric reasons. However, direct oxidative-addition of the alkylated-ligand salt (III) to $IrCl(CO)(PMe_2Ph)_2$ affords the carbene complex (X).

TABLE 3

^{1}H N.m.r. spectra of platinum, palladium, and nickel complexes

	Complex	Chemical shifts (τ) [a] and coupling constants (Hz)
(XVIII)	*trans*-PtCl(C:NCH:C(Me)S)(PEt_3)$_2$ [b]	PCH$_2$*Me*, 8·89 (q) $\vert{}^3J(PH) + {}^5J(PH)\vert$ 16; PC*H*$_2$Me, 8·27 (m); CMe, 7·60 (s); C*H*, 3·20 (s), ^4J(PtH) 14
(XIX)	[*trans*-PtCl(CNHCHC(Me)S)(PEt_3)$_2$]BF_4	PCH$_2$*Me*, 8·87 (q) $\vert{}^3J(PH) + {}^5J(PH)\vert$ 16; PC*H*$_2$Me, 8·28 (m); C*Me*, 7·40 (s); C*H*, 2·73 (s), ^4J(PtH) 14
(XII)	[*cis*-PtCl(CN(Me)CHC(Me)S)(PEt_3)$_2$]BF_4 [c]	PCH$_2$*Me*, 8·77 $\vert{}^3J(PH) + {}^5J(PH)\vert$ 14; PC*H*$_2$Me, 8·00 (m), C*Me* 7·46 (s); NMe, 5·86 (s), ^4J(PtH) 3; C*H*, 2·62, ^4J(PtH) 12
(XIII)	[*trans*-PtCl(CN(Me)CHC(Me)S)($PMePh_2$)$_2$]BF_4 [d]	P*Me*, 7·71 (t), $\vert{}^2J(PH) + {}^4J(PH)\vert$ 8, ^3J(PtH) 26; C*Me*, 8·22 (s); NMe, 6·86 (s), ^4J(PtH) 7; C*H*, 3·20 (s), ^4J(PtH) 18; P*Ph*, 2·64 (m), 2·47 (m), 2·25 (m)
(XIV)	[*trans*-PdCl(CN(Me)CHC(Me)S(PPh_3)$_2$]BF_4	C*Me*, 8·20 (s); N*Me*, 6·75 (s); C*H*, 2·87 (s); P*Ph*, 2·55 (m)
(XV)	[*trans*-PdCl(CN(Me)CHC(Me)S)($PMePh_2$)$_2$]BF_4	C*Me*, 8·18(s); P*Me*, 7·78 (t), $\vert{}^2J(PH) + {}^4J(PH)\vert$ 8; N*Me*, 6·77 (s); C*H*, 3·08 (s); P*Ph*, 2·50 (m)
(XVII)	[*trans*-PdI(CN(Me)CHC(Me)S)(PPh_3)$_2$]BF_4	C*Me*, 8·18 (s); NMe, 6·80 (s); C*H*, 3·02 (s); P*Ph*, 2·55 (m)
(XVI)	[*trans*-NiCl(CN(Me)CHC(Me)S)(PPh_3)$_2$]BF_4	C*Me*, 8·18 (s); NMe, 6·52 (s); C*H*, 2·95 (s); P*Ph*, 2·35 (m)

[a] Measured in $CDCl_3$ (XVIII, XIX, and XII) or CD_3CN (others). [b] From $^1H\{^{31}P\}$INDOR, δP, $-14{\cdot}3$ p.p.m. (rel. 85% H_3PO_4), ^2J(PP) 407 Hz. From $^1H\{^{195}Pt\}$INDOR, δPt $-$ 397·3 p.p.m. (upfield from 21·4 MHz), J(PtP) 2500 Hz. [c] From $^1H\{^{31}P\}$INDOR $\delta P_1 - 8{\cdot}3$, $\delta P_1 - 6{\cdot}1$ p.p.m. $^2J(P_1P_2) < 75$ Hz. From $^1H\{^{195}Pt\}$INDOR, δPt, -116 p.p.m. $J(PtP_1)$ 2228, $J(PtP_2)$ 3446 Hz. [d] From $^1H\{^{31}P\}$INDOR. δP. $-6{\cdot}0$ p.p.m., J(PP) 417 Hz, From $^1H\{^{195}Pt\}$, δPt, -317 p.p.m. J(PtP) 2413 Hz.

The cationic complexes (VII)—(X) are inert to ligand substitution. For example, prolonged reaction of the borofluoride salt of (VII) with an excess of iodide ion led only to anion exchange to give [$IrCl_2$(CO)(CNHCHC(Me)S)(PMe_2Ph)$_2$]I (XI).

Among d^{10} complexes, Pt(PEt_3)$_2$(PhCH:CHPh), Pt($PMePh_2$)$_4$, Pd(PPh_3)$_4$, Pd($PMePh_2$)$_4$, and Ni(PPh_3)$_4$ react with (III) in an oxidative-elimination manner to give borofluoride salts of the cations (XII)—(XVI). Prolonged reaction of the borofluoride salt of (XIV) with an excess of tetraethylammonium iodide resulted in replacement of Cl by I to give [PdI{CN(Me)CHC(Me)S}(PPh_3)$_2$]BF_4 (XVII). Similar halide exchanges have been recently reported.[9b]

Treatment of Pt(PEt_3)$_2$(PhCH:CHPh) with 2-chloro-5-methyl-1,3-thiazole gives PtCl(C:NCH:C(Me)S)(PEt_3)$_2$ (XVIII) which on protonation yields the carbene containing cation [PtCl(CNHCHC(Me)S)(PEt_3)$_2$]$^+$ (XIX).

The cyclic carbene ligands in the complexes described above, like the carbon-bonded imidazolidene derivatives of iron [15,16] and ruthenium [17] and the substituted pyran-2-ylidene complexes of chromium and molybdenum,[18] may be regarded as aromatic in nature.[19]

In the i.r. (Table 2) the cations (VII)—(X) show ν (CO) (max) in the range 2071—2089 cm^{-1}, typical of cationic Ir^{III} carbonyl complexes. These absorptions are higher than those of their neutral Ir^{III} precursors except for (IX). The cationic carbene complexes (VII)—(IX) formed by protonation show ν (NH) (max) in the range 3350—3100 cm^{-1} expected for the group $>$NH rather than that (2700—2250 cm^{-1}) corresponding to $\geqslant\overset{+}{N}H$.[20]

The pattern observed for the CH_3-P signals in the ^{1}H n.m.r. spectra of the iridium complexes (Table 2) is as expected for a *trans* arrangement of the phosphine ligands.[21,22] The two triplet signals correspond to the absence of a plane of symmetry through the PIrP axis.

Data from the ^{1}H n.m.r. spectra of the nickel, palladium, and platinum complexes is summarised in Table 3. The triplet pattern for the CH_3-P group in the spectra of (XIII) and (XV) establishes a *trans*-configuration for the methyldiphenylphosphine ligands. Complexes (XVIII) and (XIX) are assigned a *trans*-configuration based on the 1 : 4 : 6 : 4 : 1 quintet signal for the CH_3CH_2P protons.[23] The stereochemistry of (XVIII) is further confirmed by the relatively large value of ^2J(PP) which is typical of *trans*-phosphine

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ligands,[24] and the same is true for complex (XIII). However, $^{1}\mathrm{H}\{^{31}\mathrm{P}\}$ and $^{1}\mathrm{H}\{^{195}\mathrm{Pt}\}$ INDOR studies on complex (XII) (Table 3) establish the presence of two non-equivalent phosphorus nuclei and in accord with this the $^{195}\mathrm{Pt}$ signal shows a doublet of doublets, so that this complex must have a *cis*-configuration.

EXPERIMENTAL

$^{1}\mathrm{H}$ N.m.r. spectra were recorded on Varian Associates T60 and HA100 spectrometers. The $^{31}\mathrm{P}$ and $^{195}\mathrm{Pt}$ information was obtained from INDOR measurements described elswhere.[25] I.r. spectra were recorded with a Perkin-Elmer 457 spectrophotometer. Solvents were dried and distilled under nitrogen, and all operations were conducted in an atmosphere of dry oxygen-free nitrogen. The zero-valent complexes $\mathrm{Pt(PEt_3)_2(PhCH{:}CHPh)}$,[26] $\mathrm{Pt(PMePh_2)_4}$,[27] $\mathrm{Pd(PPh_3)_4}$,[28] $\mathrm{Pd(PMePh_2)_4}$,[28] and $\mathrm{Ni(PPh_3)_4}$[29] were prepared as described in the literature. The salt $\mathrm{[ClCN(Me)CHC(Me)S]BF_4}$ (m.p. 203·5—205°) was obtained in quantitative yield by treating 2-chloro-5-methyl-1,3-thiazole with $\mathrm{Me_3O^+BF_4^-}$ in dichloromethane–acetonitrile (3 : 1) (Found: C, 25·7; H, 3·0; N, 6·0. Calc. for $\mathrm{C_5H_7BClF_4NS}$: C, 25·5; H, 3·0; N, 5·9%). The $^{1}\mathrm{H}$ n.m.r. spectrum of (III) shows signals at τ 7·43 (d), C*Me*, ^{4}J(MeH) 1·1 Hz; 6·03, N*Me*; 2·22 (q), C*H*, ^{4}J(HMe) 1·1 Hz.

$\mathrm{IrCl_2(CO)(C{:}NC_6H_4S)(PMe_2Ph)_2}$ (VI) was prepared by treating $\mathrm{IrCl(CO)(PMe_2Ph)_2}$ (0·40 g, 0·75 mmol) with a slight excess of freshly distilled 2-chlorobenzthiazole (IIa) in refluxing benzene (20 ml) for 24 h. Solvent was removed under vacuum to give a pale yellow oil which was triturated with diethyl ether (20 ml) affording a white solid. Recrystallisation from methylene chloride–cyclohexane (1 : 5, 10 ml) yielded white *crystals* (Table 1).

The complexes $\mathrm{IrCl_2(CO)(C{:}NC_6H_4O)(PMe_2Ph)_2}$ (V) and $\mathrm{IrCl_2(CO)(C{:}NCH{:}C(Me)S)(PMe_2Ph)_2}$ (IV) were prepared similarly from reactions of $\mathrm{IrCl(CO)(PMe_2Ph)_2}$ with 2-chlorobenzoxazole (IIb) and 2-chloro-5-methyl-1,3-thiazole (I), respectively.

$\mathrm{[IrCl_2(CO)(CNHC_6H_4S)(PMe_2Ph)_2]X}$ ($\mathrm{X = ClO_4^-, BF_4^-}$) (IX) was prepared by treating (VI) (0·10 g, 0·14 mmol) with an excess of perchloric (or fluoroboric) acid in methylene chloride–ethanol (1 : 1, 5 ml). The solution was stirred vigorously for 15 min and the resulting white *solid* (Table 1) was recrystallised from a methylene chloride–ethanol–cyclohexane mixture. The carbene complexes, $\mathrm{[IrCl_2(CO)(CNHC_6H_4O)(PMe_2Ph)_2]X}$ ($\mathrm{X = ClO_4^-, BF_4^-}$) (VIII), and $\mathrm{[IrCl_2(CO)(CNHCHC(Me)S)(PMe_2Ph)_2]BF_4}$ (VII) were prepared in a similar fashion.

Synthesis of $\mathrm{[IrCl_2(CO)(CN(Me)CHC(Me)S)(PMe_2Ph)_2]BF_4}$ (X).—This compound was prepared by treating $\mathrm{IrCl(CO)(PMe_2Ph)_2}$ (0·40 g, 0·75 mmol) with a slight excess of the borofluoride salt of *N*-methyl-2-chloro-5-methyl-1,3-thiazole (III) in refluxing benzene (20 ml) for 16 h. The resulting white *solid* was recrystallised from methylene chloride–benzene–hexane mixture.

Reaction of (VII) *and Potassium Iodide*.—The complex $\mathrm{[IrCl_2(CO)(CNHCHC(Me)S)(PMe_2Ph)_2]I}$ (XI) was prepared by reacting (VII) (0·20 g, 0·27 mmol) with a slight excess of potassium iodide in 20 ml of refluxing methylene chloride–ethanol (1 : 3) for 16 h. Solvent was removed *in vacuo* and the resulting solid was dissolved in methylene chloride, filtered to remove the excess of potassium iodide, and the hexane then added to give white *crystals*.

Treatment of (IX) *with Base*.—The compound $\mathrm{[IrCl_2(CO)(CNHC_6H_4S)(PMe_2Ph)_2]BF_4}$ (0·10 g, 0·13 mmol) in methylene chloride (10 ml) was treated with a slight excess of sodium hydroxide in methanol (1 ml). After vigorous stirring (15 min), the solvent was removed under vacuum, and the resulting product dissolved in methylene chloride and filtered to remove sodium tetrafluoroborate. Addition of hexane gave white *crystals* of (VI).

The Complex $\mathrm{PtCl(C{:}NCH{:}C(Me)S)(PEt_3)_2}$ (XVIII).—This complex was prepared by treating $\mathrm{Pt(PhCH{:}CHPh)(PEt_3)_2}$ (0·68 g, 1·11 mmol) with a slight excess of freshly distilled 2-chloro-5-methyl-1,3-thiazole (I) in degassed hexane (20 ml). After stirring for 20 min, the solvent was removed under vacuum and the resulting pale yellow solid was carefully sublimed (70°, 0·05 mmHg) to separate stilbene from white *crystals* of (XVIII).

Treatment of (XVIII) *with* $\mathrm{HBF_4}$.—The compound $\mathrm{[PtCl(CNHCHC(Me)S)(PEt_3)_2]BF_4}$ (XIX) was prepared from a reaction between (XVIII) (0·16 g, 0·28 mmol) and an excess of fluoroboric acid in methylene chloride–ethanol (1 : 1, 5 ml). The solution was stirred vigorously for 15 min and the resulting white *solid* was recrystallised from methylene chloride–hexane.

$\mathrm{[PtCl(CN(Me)CHC(Me)S)(PEt_3)_2]BF_4}$ (XII) was prepared by reacting $\mathrm{Pt(PhCH{:}CHPh)(PEt_3)_2}$ (0·70 g, 1·14 mmol) with a slight excess of (III) in tetrahydrofuran (10 ml) for 2 h. The resulting *solid* was recrystallised from methylene chloride–hexane.

The complexes $\mathrm{[PtCl(CN(Me)CHC(Me)S)(PMePh_2)_2]BF_4}$ (XIII), $\mathrm{[PdCl(CN(Me)CHC(Me)S)(PPh_3)_2]BF_4}$ (XIV), $\mathrm{[PdCl(CN(Me)CHC(Me)S)(PMePh_2)_2]BF_4}$ (XV), and $\mathrm{[NiCl(CN(Me)CHC(Me)S)(PPh_3)_2]BF_4}$ (XVI) were prepared in a similar manner from reaction of (III) with $\mathrm{Pt(PMePh_2)_4}$, $\mathrm{Pd(PPh_3)_4}$, $\mathrm{Pd(PMePh)_2)_4}$, and $\mathrm{Ni(PPh_3)_4}$ respectively.

Reaction of (XIV) *with Tetraethylammonium Iodide*. The complex $\mathrm{[PdI(CN(Me)CHC(Me)S)(PPh_3)_2]BF_4}$ (XVII) was prepared from a reaction of (XIV) (0·25 g, 0·29 mmol) and a slight excess of tetraethylammonium iodide in refluxing methanol (20 ml). After 16 h the yellow *solid* was filtered and recrystallised from methylene chloride–hexane.

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