Transition-metal Complexes with $(CF_3)_2C=N^-$ as Ligand, and a Tautomeric Hydrogen Transfer from Metal to Ligand
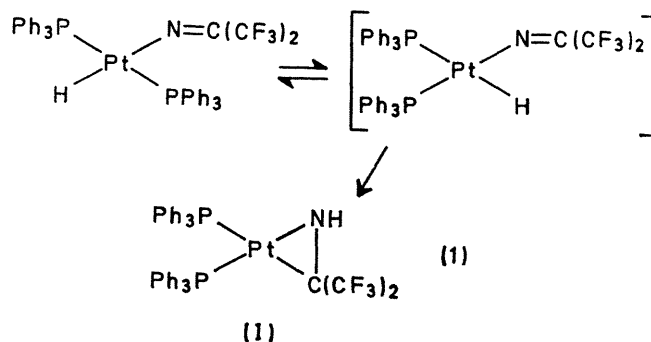
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Summary Reactions of appropriate metal chlorides and $(CF_3)_2C=NLi$ (RLi) afford the novel ketimides $(\pi\text{-}C_5H_5)_2\text{-}$Ti(R)Cl, $(Ph_3P)_3RhR$, *cis*-$(Ph_3P)_2Pt(R)Cl$, *trans*-$(Ph_3P)_2$-Pt(R)H, *cis*-$(Me_2PhP)_2Pt(R)Cl$, *cis*-$(Me_2PhP)_2PtR_2$, and *trans*-$(Me_2PhP)_2Pt(R)H$; and *trans*-$(Ph_3P)_2Pt$-(R)H is isomerised by heating with Ph_3P in benzene to yield $(Ph_3P)_2Pt[HNC(CF_3)_2]$.

THE transition-metal complex chemistry of the amido-ligand (R_2N^-) has recently been extensively explored, with interesting consequences—*e.g.*, for $Ti^{3+},$[1] $Mo^{6+},$[2] and $Fe^{3+};$[3] data are broadly limited to early transition metals. Results on the imido-ligand $(R^1R^2C=N^-)$ are as yet much more sparse: complexes of $Ti^{4+},$[4] $Zr^{4+},$[4] $Hf^{4+},$[4] $Mo^{2+},$[5] $W^{2+},$[5] and Fe^+[6] have been reported.

We now draw attention to the ligand $(CF_3)_2C=N^-$, which we have generally attached to the transition metal by means of the explosive (at $25°)$[7] $(CF_3)_2C=NLi$ and the appropriate metal chloride at *ca.* $6°$ using benzene as solvent. Several features are already apparent: (i) stable monomeric complexes are accessible (see Table), notably among late transition metals; (ii) the ligand confers increased volatility on complexes [note the ready sublimation of the Ti ketimide (the first of these compounds to be made, in collaboration with M. R. Collier), whereas the simpler ketimides $(\pi\text{-}C_5H_5)_2Ti(N=CR_2)Cl$ $(R = Bu^t$ or $Ph)$[4] of comparable molecular weights sublime with difficulty at *ca.* $160°/10^{-3}$ mmHg], as should become especially significant for $M[N=C\text{-}(CF_3)_2]_n$; (iii) the complexes are air-stable (*cf.* generally the ready hydrolysis of metal amides and imides) and soluble in non-polar solvents; (iv) spectroscopic data on some of the

Pt^{2+} derivatives suggest that $(CF_3)_2C=N^-$ exerts a relatively high *trans*-influence, probably comparable[8] to NO_2^-; and (v) trends in $\nu(C=N)$ point to the possibility of $(d \rightarrow \pi^*)$ π-bonding in the d^8 complexes.

(1)

An unexpected difference was observed in the reactions of $(CF_3)_2C=NLi$ with *cis*-$(Ph_3P)_2PtCl_2$ and *cis*-$(Me_2PhP)_2$-$PtCl_2$: with the former dichloride no bis-ketimide was obtained even when using more than 2 moles of the lithium reagent, whereas *cis*-$(Me_2PhP)_2Pt[N=C(CF_3)_2]_2$ was the principal product of equimolar interaction of the lithium reagent and the latter dichloride.

As *cis*-$(Ph_3P)_2Pt[N=C(CF_3)_2]_2$ proved inaccessible by the lithium route, the reaction of $(Ph_3P)_3Pt$ and $(CF_3)_2C=N$·-$N=C(CF_3)_2$ was examined. At *ca.* $10°$ in benzene, there was an instant discharge of the yellow colour of $(Ph_3P)_3Pt$.

White, sparingly benzene-soluble crystals were isolated, believed to be of $[(Ph_2P)_2Pt]_n$ on the basis of analysis.† There may be analogy with (i) the pyrolysis of $(Ph_3P)_2$-

$$Pt\begin{array}{c} \diagup OCO \\ \diagdown OCO \end{array}\bigg|$$
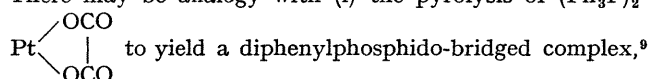
to yield a diphenylphosphido-bridged complex,[9] and (ii) the compound $[(Ph_2P)PtCl]_m$.[10]

An alternative route to $(Ph_3P)_2Pt[N=C(CF_3)_2]H$ proved unsuccessful: this was based on the observation[11] that acid imides such as succinimide add oxidatively to Pt^0

of tautomerism in a Ru complex.[14] However, equation (1) provides the first illustration of an isomerisation involving a hydrogen transfer from metal to ligand. Such tautomerism is often invoked to account *inter alia* for the transition-metal-catalysed isomerisation of olefins. Reaction (1) has some parallel, but in a reverse sense, to the isomerisation of certain π-chloro-olefin–metal complexes to σ-alkenyl-metal chlorides [*e.g.*, $(Ph_3P)_2Pt(ClCF:CF_2) \rightarrow (Ph_3P)_2Pt$-$(CF:CF_2)Cl$].[15] Also relevant are experiments with $CH_2:CHCN$ and $C_2(CN)_4$.[16]

TABLE[a]

Compound $[R=N:C(CF_3)_2]$	Appearance and m.p.	$\nu(C=N)$ (Nujol mulls) (cm^{-1})	Other selected spectral data
$(\pi\text{-}C_5H_5)_2Ti(R)Cl$[b,c]	yellow,194—195° (dec.)	1715	—
$(Ph_3P)_3RhR$	yellow, 104° (dec.)	1668	—
$cis\text{-}(Ph_3P)_2Pt(R)Cl$[d]	white, 245—250° (dec.)	1673	^{31}P n.m.r. (CDCl$_3$), a doublet.
$trans\text{-}(Ph_3P)_2Pt(R)H$	yellow, 139—140° (dec.)	1663	ν(Pt–H), 2146 cm^{-1}; ^1H n.m.r. (C$_6$D$_6$): H(Pt) at τ 22·8, J(Pt–H) 748 Hz, J(P–H) 16 Hz; ^{31}P n.m.r. (C$_6$D$_6$): singlet + 86·6 p.p.m. from P$_4$O$_6$, J(Pt–P) 3·15 KHz.
$cis\text{-}(Me_2PhP)_2Pt(R)Cl$[b]	white, 128—130°	1670	—
$cis\text{-}(Me_2PhP)_2PtR_2$[b,e]	yellow, 102—104°	1675, 1650	^1H n.m.r. (CDCl$_3$): Ph τ 2·5, Me 3 doublets (intensity 1:4:4:1) centred at τ 8·7, J(P–H) 11 Hz, J(Pt–H) 29 Hz; ^{31}P n.m.r. (CDCl$_3$): singlet + 140·2 p.p.m. from P$_4$O$_6$, J(Pt–P) 2·93 KHz.
$trans\text{-}(Me_2PhP)_2Pt(R)H$[b] ..	yellow, 48—50°	1663	ν(Pt–H), 2115 cm^{-1}; ^1H n.m.r.: 3 triplets centred on τ 9·3 H(Pt) at τ 24·3, J(P–H) 17 Hz.

[a] Satisfactory elemental analyses were obtained on all compounds, which were obtained from $(CF_3)_2C=NLi$ in 60—80% yield [except $(Me_2PhP)_2Pt(R)Cl$, 15%];
[b] Parent molecular ion observed in mass spectrum;
[c] Sublimed readily at $< 85°/10^{-3}$ mmHg;
[d] Also in low yield from $cis\text{-}(Ph_3P)_2PtCl_2 + (CF_3)_2C=NH + Et_3N$;
[e] Found: M, 840 (in CHCl$_3$, isopiestically). $C_{22}H_{22}F_{12}N_2P_2Pt$ requires M, 799.

complexes. Interaction of $(Ph_3P)_3Pt$ and $(CF_3)_2C=NH$ gave the recently described[12] ring compound (I), which could not be isomerised thermally or photolytically. The reverse reaction was, however, demonstrated, (I) being obtained (equation 1) by heating the *trans*-hydride in benzene with Ph_3P; the presumed intermediate *cis*-complex was not isolated. Many examples of hydrogen transfer from ligand to metal are now known,[13] as is a case

† *Note added in proof:* Further studies, now in hand, indicate that the suggested formula is incorrect and that the material probably arises from the presence of impurities in the starting azine.[7]

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