Transition-metal Chemistry of Dichloromethylene(dimethyl)ammonium Chloride; *C*-Chlorocarbene Complexes†

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Summary *C*-Chlorocarbene d^6 complexes of Cr^0, Mn^I, and Rh^{III}, (I)—(V), have been obtained from $[Me_2NCCl_2]^+Cl^-$ and the appropriate transition metal complex precursor, by four procedures (*a*, *a'*, *a''*, or *b*); alternative reaction pathways (*c* or *d*) lead to other species, including the electron-rich cluster compound $[Co_3(CO)_9CNMe_2]$.

An important development in the chemistry of carbene–transition-metal complexes has been the conversion of certain *C*-alkoxycarbene–metal species, $[ML_n\{C(OR^1)R^2\}]$, into carbynemetal halides $[M(Hal)L_m(CR)]$, by treatment with boron or related metal halides.[1] There has been speculation that *C*-halogenocarbenemetal compounds, $[ML_n\{C(Hal)R\}]$, are implicated as intermediates, but attempts to isolate them have failed.[2] We now report on some *C*-chlorocarbenemetal d^6 complexes of Cr^0, Mn^I, and Rh^{III}, (I)—(V), obtained by four types of reactions (*a*, *a'*, *a''*, and *b*; see Scheme) from dichloromethylene(dimethyl)ammonium chloride, $[Me_2NCCl_2]^+Cl^-$, and an appropriate transition-metal complex. Such complexes are of further interest as providing examples of relatively stable carbenemetal species bearing an electronegative substituent at C_{carb} and

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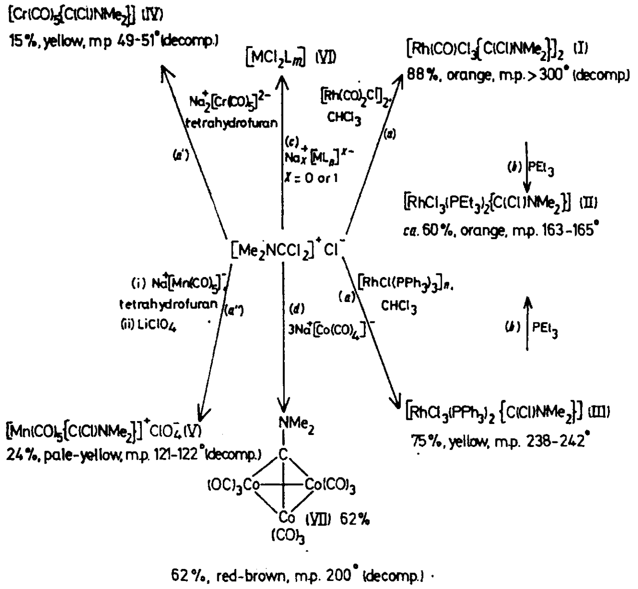
may be of value as precursors not only of carbynemetal complexes but also of other carbene–metal species bearing a variety of substituents at C_{carb}.



Scheme

The *C*-chlorocarbenemetal syntheses illustrated in the Scheme refer to: *a*, three-fragment oxidative-addition; *a'*, salt elimination; *a''*, salt elimination with concomitant two-fragment oxidative-addition; and *b*, ligand substitution. We have observed two further modes of reaction, *c* and *d*, between $[Me_2NCCl_2]^+Cl^-$ and other transition metal compounds. Mode *c* is an oxidative-elimination without carbene incorporation, and has been observed ***inter alia*** with $Na_x^+[ML_n]^{x-}$ = $[Ru(CO)_3(PPh_3)_2]$, *trans*-$[Ir(CO)Cl(PPh_3)_2]$, and $Na[Co(CO)_3(PPh_3)]$. Mode *d* led to the unusual electron-rich cluster compound (VII). Reactions related to *a*[3] and *a'*[4] have previously been observed for $[Me_2NCHCl]^+Cl^-$, a convenient source of secondary carbenemetal complexes $[ML_n\{C(H)NMe_2\}]$.

Pathway *a''* is now shown significantly to extend the range of available secondary carbenemetal complexes: *e.g.*, using $[Me_2NCHCl]^+Cl^-$, $[M(\eta^5\text{-}C_5H_5)(CO)_3\{C(H)NMe_2\}]^+[M(\eta^5\text{-}C_5H_5)(CO)_3]^-$ [M = Mo, 81%, yellow, m.p. 140° (decomp.); M = W, 87% yellow-brown, m.p. 127—128° (decomp.); *cis*-$[Mn(CO)_4Cl\{C(H)NMe_2\}]$, 22%, yellow, m.p. 91—93°; *cis*-$[Re(CO)_4Cl\{C(H)NMe_2\}]$, 58%, fawn, m.p. 96—98°; and $[Co(CO)_2Cl(PPh_3)\{C(H)NMe_2\}]$, 45%, yellow, m.p. 178—180°. These compounds are also of interest as potential precursors for carbynemetal complexes (*cf.*, ref. 5).

Pathway *c* is less common for $[Me_2NCHCl]^+Cl^-$ than the perchloro-analogue, but has been observed with $[Pt(PPh_3)_3]$ and *trans*-$[Ir(CO)Cl(PMePh_2)_2]$.

Compounds (I)—(V) and (VII) gave satisfactory analytical and spectroscopic data. The ν(CCl) in $[ML_n\{C(Cl)\text{-}NMe_2\}]$ assignment [ν(CCl), cm^{-1}: (I), 860; (II), 807; (IV), 779; and (V), 826] is supported by the absence of this band in the corresponding $[ML_n\{C(H)NMe_2\}]$. The ν(CN) for C_{carb} is closely similar[3] for the two types of carbene–metal complexes [ν(CN), cm^{-1}: (I), 1578; (II), 1533; (III), 1591; (IV), 1520; and (V), 1566]. The *C*-chlorocarbenemetal complexes, especially (IV) and (V), are unstable in solution, slow decomposition occurring at room temperature.

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