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Preliminary communication

Metal complexes of cyanocarbons
XIV*. Dicyanomethyl and monocyanoketeniminato complexes of some noble metals

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SUMMARY

Reactions of sodium dicyanomethanide with chloro-substituted noble metal substrates give complexes containing the C_3HN_2 moiety. Spectroscopic data suggest that some of the new complexes contain a dicyanomethyl ligand, M–CH(CN)$_2$, whereas others are monocyanoketeniminato complexes, M–N=C=CH(CN).

Following our study[1] of the reactions of the tricyanomethanide ion, $C(CN)_3^-$, with some noble metal substrates in which dicyanoketeniminato complexes, *i.e.* containing the M–N=C=C(CN)$_2$ linkage, were prepared, we have investigated related reactions of the dicyanomethanide ion, $CH(CN)_2^-$, for purposes of comparison with $C(CN)_3^-$ chemistry. Some dicyanomethyl complexes of cobalt have been recently reported[2,3], and all of these are believed to contain the Co–CH(CN)$_2$ linkage.

Addition of ethanolic solutions of sodium dicyanomethanide to benzene solutions of $MCl(CO)(PPh_3)_2$ (M = Rh, Ir) gave, after work-up, bright yellow monomolecular products $M(C_3HN_2)CO(PPh_3)_2$. The iridium complex reacts with π-acids such as tetracyanoethylene and fumaronitrile to give 1/1 adducts, but it does not react with dioxygen. The C_3HN_2 moiety in $Ir(C_3HN_2)(CO)(PPh_3)_2$ is displaced by bromide ion and is also cleaved by HCl.

Treatment of a methanol solution of $PdCl_2(NCPh)_2$ with ethanolic $NaCH(CN)_2$, followed by addition of $(Ph_4As)Cl$, gave the white compound $(Ph_4As)_2[Pd(C_3HN_2)_4]$. The same compound was obtained from $Na_2[PdCl_4]$. From the platinum complexes $PtCl_2(PPh_3)_2$ and $PtHCl(PPh_3)_2$, on treatment with $NaCH(CN)_2$ at room temperature, were obtained $PtCl(C_3HN_2)(PPh_3)_2$ and $PtH(C_3HN_2)(PPh_3)_2$, respectively. Reaction of

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*For Part XIII see ref. 1.

TABLE 1

NEW COMPLEXES [a] DERIVED FROM SODIUM DICYANOMETHANIDE AND SOME INFRARED DATA [b]

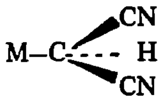
Compound	*ν(C≡N)*	*ν(C≡O)*	*ν(Other)*
$Ir(C_3HN_2)CO(PPh_3)_2$	2195m, 2122vs	1970s	1355 (N=C=C sym)
$Ir(C_3HN_2)CO(TCNE)(PPh_3)_2$	2220m, 2195m, 2135s	2076s	
$Ir(C_3HN_2)CO(FUMN)(PPh_3)_2$ [c]	2220m, 2201m, 2148s	2042s	
$Rh(C_3HN_2)CO(PPh_3)_2$	2190m, 2120vs	1985s	1355 (N=C=C sym)
$PtCl(C_3HN_2)(PPh_3)_2$	2201vs, 2184s		
$PtH(C_3HN_2)(PPh_3)_2$	2208m		2125m (Pt–H) [d]
$[Ph_4As]_2[Pd(C_3HN_2)_4]$	2200s		

[a] Satisfactory analytical results for C, H, and N have been obtained for all the complexes. [b] Recorded in Nujol mulls and given in cm^{-1}. [c] FUMN is fumaronitrile. [d] Our assignment of the 2208 cm^{-1} band as ν(C≡N) and the 2125 cm^{-1} band as ν(Pt–H) in this complex, and not *vice versa*, is based on the fact that both bands are of the same intensity and of medium strength. If the complex contains a Pt–N=C=CH(CN) linkage, then the 2125 cm^{-1} band would correspond to the ν(N=C=C) asymmetric frequency. However, such bands in previously prepared iridium and platinum keteniminato complexes (Ref. 1 and 4) are very strong in intensity. Platinum–hydrogen stretching frequencies in complexes of the type $PtHX(PPh_3)_2$ are of medium strength.

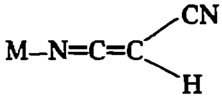
$PtHCl(PPh_3)_2$ and $NaCH(CN)_2$ at 70°C produced the dicyano-compound $Pt(CN)_2(PPh_3)_2$.

Attempts to prepare complexes containing the $CH(CN)_2$ moiety via oxidative addition of malononitrile, $CH_2(CN)_2$, with $RhH(CO)(PPh_3)_3$, $RhCl(CO)(PPh_3)_2$, $IrCl(CO)(PPh_3)_2$, and $Ni(CO)_2(PPh_3)_2$ were not successful.

Some pertinent infrared data for the new complexes are given in Table 1. Two bonding modes, I and II, may be envisioned.



(I)



(II)

The previously reported cobalt complexes of $CH(CN)_2^-$, one of which was shown by X-ray crystallography to contain a cobalt–carbon bond[2], exhibit ν(C≡N) at ca. 2200 cm^{-1}. The palladium and platinum complexes reported herein probably also are dicyanomethyl complexes (structure I) since ν(C≡N) values are near 2200 cm^{-1}. Also, the ^{1}H NMR spectrum of $PtH(C_3HN_2)(PPh_3)_2$ shows a triplet of doublets centered at τ 20.8 in the high field region with J(P–H) 15 Hz and J(H–H) 3 Hz, thus suggesting a *trans* arrangement of phosphine ligands. The coupling of the hydridic proton with the C_3HN_2 proton seems more likely for structure I than for structure II. The relatively low platinum–hydrogen stretching frequency of 2125 cm^{-1} (see footnote *d* of Table 1) in the infrared spectrum of $PtH(C_3HN_2)(PPh_3)_2$, when compared with ν(Pt–H) of complexes of the type $PtHX(PPh_3)_2$ [5] (X = Cl, 2220; X = NO_2, 2180; X = CN, 2075), suggests a fairly high *trans* effect for the dicyanomethyl group.

In contrast to the platinum and palladium complexes mentioned above, and the previously reported dicyanomethyl complexes of cobalt, the four rhodium and iridium complexes listed in Table 1 appear to be of structure II with a metal—nitrogen bond as deduced from the presence of very strong absorption bands in the 2120—2150 cm^{-1} range of the infrared spectrum. These energies are somewhat lower than those previously reported for iridium and platinum keteniminato complexes derived from tetracyanoethylene and the tricyanomethanide ion[1,4], but certainly of much lower energy and of greater intensity than would be expected for a dicyanomethyl formulation.

We have not as yet observed any tendency for the dicyanomethyl or monocyano-keteniminato complexes reported herein to isomerize to the other form. A wider variety of complexes containing the $CH(CN)_2$ group is being prepared in order to assess further the bonding tendencies of this versatile ligand.

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