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Preliminary communication

CYANOALKYL COMPLEXES OF TRANSITION METALS

III. REACTIONS OF ORGANOMETALLIC COMPLEXES OF PALLADIUM AND PLATINUM WITH SODIUM DICYANOMETHANIDE

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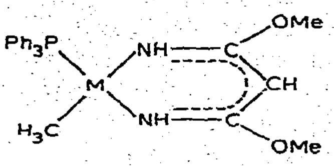
Summary

Reactions of $MI(CH_3)(PPh_3)_2$ or $MCl(CH_2COR)(PPh_3)_2$ (M = Pd, Pt) with sodium dicyanomethanide in methanol gave novel metal complexes. Spectroscopic data suggest that these complexes contain either an imino-ether chelate ring or a carbon—carbon chelate ring which was derived from $CH(CN)_2^-$.

Recently, reactions of transition metal complexes with dicyanomethanide ion, $CH(CN)_2^-$, have been reported [1—3]. The product obtained in these reactions contained either a $M—N=C=C(CN)_2$ or a $M—CH(CN)_2$ linkage. During our study on cyanoalkyl complexes of transition metals [4] we found novel reactions in which an imino—ether chelate ring or a carbon—carbon chelate ring is derived from $CH(CN)_2^-$.

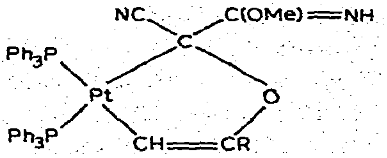
A methanol solution (50 ml) of $NaCH(CN)_2$ prepared by the mixing of NaOMe (540 mg) and $CH_2(CN)_2$ (660 mg) in dry methanol was added to a methanol suspension $MI(CH_3)(PPh_3)_2$ (Pd: 2.0 g, Pt: 1.0 g). After the mixture had been stirred overnight under nitrogen at room temperature, the product was filtered off, washed with ether and recrystallized from acetone (Pd) or $CHCl_3/(C_2H_5)_2O$ (Pt) giving the complexes Ia or Ib, respectively.

A suspension of $PtCl(CH_2COR)(PPh_3)_2$ ($R = CH_3$: 2.0 g, R = Ph: 2.0 g) in methanol was treated with a methanol solution of $NaCH(CN)_2$ prepared as described above. After stirring for 3 h (R = Ph) or overnight ($R = CH_3$), a yellow product was obtained in each case. It was recrystallized from $CHCl_3/(C_2H_5)_2O$ giving the yellow complexes IIa or IIb. On the other hand, the palladium analogs gave only the pale yellow complex (III) under similar conditions.



(Ia) M = Pd: 30%, m.p. 159—163° (dec.)

(Ib) M = Pt: 70%, m.p. 202—205° (dec.)



(IIa) R = CH_3: 35%, m.p. 230—235° (dec.)

(IIb) R = Ph: 70%, m.p. 235—238° (dec.)

$PdCl[CH(CN)_2](PPh_3)_2$

(III) Pd: 30% m.p. 170—172° (dec.)

TABLE 1

INFRARED DATA [a]

	M	ν(NH)	ν(CN)	ν(N=C)	ν(C=C)	Other	
Ia	Pd	3380 3350		1609	1536	b	
Ib	Pt	3370 3360		1605	1537	b	
IIa	Pt	3380	2190	1574	1511	1280 1273	ν(=C—O) ν(=C—O)
IIb	Pt	3374	2196	1555	1500	1272 1248	ν(=C—O) ν(=C—O)
III	Pd		2235 2230			307	ν(Pd—Cl)

[a] All the complexes in Table 1 gave satisfactory analytical results for C, H, and N. Measured in Nujol and HCB mulls (cm^{-1}). [b] Several bands appeared in the region 1100—1300 cm^{-1}.

TABLE 2

NMR DATA [a]

	M	τ(CH$_3$)	τ(NH)	τ(OMe)	τ(CH)
Ia	Pd	9.79 d 4.0 J(P—H)	4.70(br) s 5.85(br) s	6.26 s 6.85 s	6.02 s
Ib	Pt	9.68 d [b] 4.0 J(P—H) 68.5 J(Pt—H)	4.03(br) s 5.15(br) s	6.24 s 6.84 s	5.82 s [c]
IIa	Pt	7.99(br) s	4.45(br) s	7.10 s	4.30 dd [b] 9.5 J(P—H) (*cis*) 24.5 J(P—H) (*trans*) ~40 J(Pt—H)
IIb	Pt	*d*	4.20(br) s	7.07 s	3.98(dd) [b] 8.5 J(P—H) (*cis*) 23.0 J(P—H) (*trans*) 42.5 J(Pt—H)
III	Pd				7.50(*t*) 7.0 J(P—H)

[a] Abbreviations are: s, singlet; d, doublet; t, triplet; dd, a doublet of doublets; (br), broad. Measured in $CDCl_3$; τ (ppm) J (Hz). [b] J(^{195}Pt—H) was observed. [c] An ill-resolved triplet. [d] τ(Ph) 3.04 s. τ(Ph) of PPh_3 appeared at ~2.6 for all the complexes studied here.

IR and NMR data for the new complexes are summarized in Table 1 and Table 2. These spectroscopic data support the assignment of the structures mentioned above. The result obtained here is different from that reported by Baddley et al. [3]. The mechanism of formation of the complexes (I) and (II) is not clear yet, but evidently methanol plays an important role in our reactions. The complex (I) might be prepared through the side-on coordination of a nitrile group as suggested by Clark et al [5]. For complex (II), we assume that the formation of an enolate anion from the CH_2COR group is important. We have not obtained any keteniminato complex so far. Reactions of other organometallic complexes of transition metals with $CH(CN)_2^-$ are under investigation.

References

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Erratum

J. Organometal. Chem., Vol. 69, No. 1 (April 2nd, 1974)

Page 84, line 6 from the bottom should read:

complexes should differ little in their rates of formation and k_2/k_{-2} vs. k'_2/k'_{-2}

Publisher's note

The following Annual Survey articles covering the year 1972:

- Transition Metal Organic Chemistry; Physical Methods and Results of General Interest 1972; by P.S. Braterman
- Copper, Silver and Gold; by E. Singleton
- Nickel, Palladium and Platinum; by E. Singleton

will appear in the final issue of *Organometallic Chemistry Reviews B*, vol. 10, no. 2 (June 1974).

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