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Cyanoalkyl Complexes of Transition Metals. VI. Preparation of Imino Ether Complexes of Palladium Containing a Cyanomethyl or a Dicyanomethyl Group

K. SUZUKI and S. NAKAMURA

Inorganic Chemistry Laboratory, Faculty of Science, Nagoya University, Chikusa, Nagoya, Japan 464

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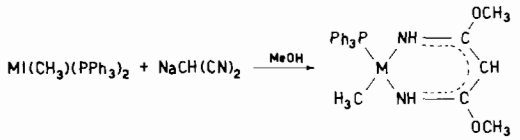
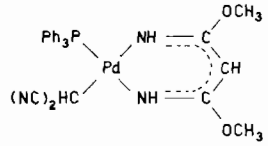
In a previous paper [1] we have shown that sodium dicyanomethanide reacts with $MI(CH_3)(PPh_3)_2$ (M = Pd, Pt) to yield an imino ether complex in methanol. This work is now extended to a study of the related systems $PdXY(PPh_3)_2$ (X = Y = Cl, X = Cl, Y = CH_2CN).



To a methanol suspension of $PdCl_2(PPh_3)_2$ was added a methanol solution of sodium dicyanomethanide prepared by adding sodium and malononitrile to dry methanol. After the mixture had been stirred overnight under nitrogen at room temperature, the reaction product was filtered, washed with water and methanol and then recrystallized from chloroform–diethyl ether to give a yellow compound (I). *Anal.* Found: C, 55.73; H, 4.53; N, 9.56. Required for $C_{26}H_{25}N_4O_2PPd$: C, 55.48; H, 4.48; N, 9.95%. Similar treatment of $PdCl(CH_2CN)(PPh_3)_2$ [2] with sodium dicyanomethanide in methanol gave a yellow compound (II). *Anal.* Found: C, 56,05; H, 4.92; N, 7.56. Required for $C_{25}H_{26}N_3O_2PPd$: C, 55.81; H, 4.87; N, 7.80%.

The complexes (I) and (II) are stable in air and soluble in common organic solvents. The infrared spectrum of (I) shows two sharp bands at 3350 and 3395 cm^{-1} assignable to ν(NH) together with two strong bands at 1600 and 1530 cm^{-1} which are ascribed to ν(N=C) and ν(C=C) respectively. In addition to these bands, there is also a strong band at 2210 cm^{-1} assignable to ν(CN). These spectral observations imply that (I) contains both imino ether and nitrile groups. The ^1H nmr spectrum of (I) is shown in Fig. 1. As expected, two NH protons appeared as a broad singlet at τ 4.3(1H) and 6.4 (1H) respectively. Moreover, an apparent triplet at τ 5.93 (1H) and two sharp singlets at τ 6.25(3H) and 6.75(3H) can be assigned to a methine and two methoxy protons of a new ligand system $-CH(C(OCH_3)=NH)_2$ which is probably formed by attack of methanol at the coordinated nitrile as reported in other systems [1, 3, 4]. Finally, a doublet at τ 8.05(1H) is assigned to the methine proton of a $Pd-CH(CN)_2$ moiety since the proton can couple with a phosphorus atom coordinated to palladium. The band assigned to ν(CN) mentioned above also supports the coordination of a dicyanomethyl group. Thus all these spectral data, together with elemental analyses, allow us to formulate (I) as an imino ether chelate containing a $Pd-CH(CN)_2$ moiety:



The spectral data of (II) are quite similar to those of (I), indicating that (II) is also an imino ether com-

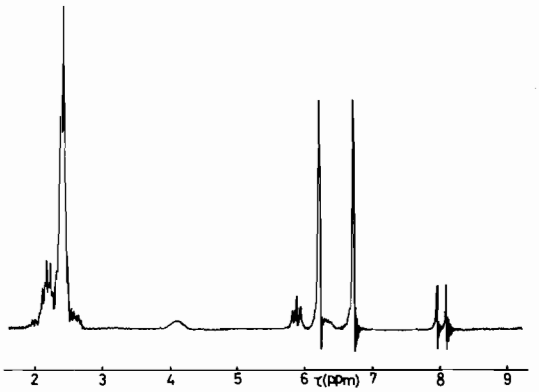


Fig. 1. ^1H nmr spectrum of $Pd(CH(CN)_2)(PPh_3)(NH=C(OCH_3))_2CH$.

TABLE I. Spectral Data of $Pd(R)(PPh_3)(NH=C(OCH_3))_2CH$ [R = $CH(CN)_2$, CH_2CH].[a]

	$CH(CN)_2$	CH_2CN
ν(NH)	3350 3395	3340 3360
ν(N=C)	1600	1606
ν(C=C)	1530	1533
ν(CN)	2210	2190
τ(Pd–R)	8.05d $^3J(PH)$ = 8.0 Hz	8.98d $^3J(PH)$ = 6.0 Hz
τ(CH)	5.93t $^4J(HH)$ = 3.0 Hz	5.98t $^4J(HH)$ = 3.0 Hz
τ(NH)	4.1brs 6.4brs	4.3brs 6.0brs
τ(OCH_3)	6.25s 6.75s	6.27s 6.82s

[a]I.R. was measured in Nujol and HCB mulls (cm^{-1}). ^1H nmr was measured in $CDCl_3$ using TMS as internal standard at room temperature. Abbreviations are: s, singlet; d, doublet; t, triplet; brs, broad singlet.

plex although it contains a cyanomethyl in place of a dicyanomethyl group.

We also examined the reaction of *cis*-$PtI_2(PPh_3)_2$ with $NaCH(CN)_2$ in methanol. However the expected imino ether complex was not obtained. Instead, the ^1H nmr spectrum of the reaction product showed a doublet of doublets at τ 8.42 suggesting the formation of *cis*-$Pt(CH(CN)_2)_2(PPh_3)_2$. Reactions of other platinum complexes with $NaCH(CN)_2$ are under investigation.

References

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