

Preliminary communication

**ADDUCTS OF A PALLADIUM(II) DERIVATIVE CONTAINING A
 σ-BONDED α-DIIMINO GROUP WITH TRANSITION METALS. A NEW
 CLASS OF BIMETALLIC COMPLEXES**

B. CROCIANI, M. NICOLINI

*Centro Chimica Tecnologia Composti Metallorganici Elementi Transizionali, U. N. R.
 Venezia (Italy) and Istituto di Chimica Generale dell' Università, Padova (Italy)*

and R. L. RICHARDS*

School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ (Great Britain)

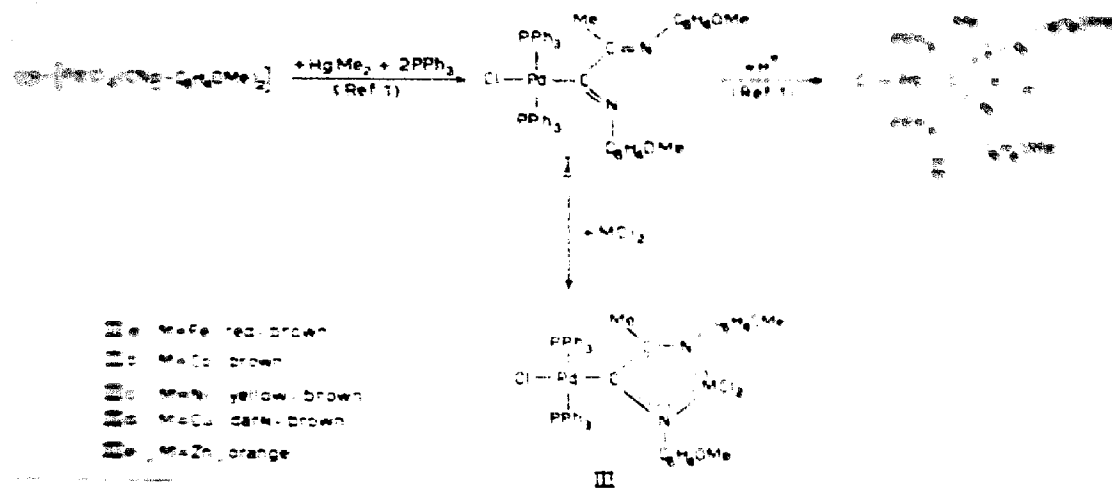
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Summary

The characterisation of 1:1 adducts of $[PdCl_2(C(NC_6H_5)_2OMe)_2]$ and MCl_2 ($M = Fe, Co, Ni, Cu$ and Zn) is described.

In a previous paper we have described the preparation of palladium(II) complexes containing α-diimino groups and their facile protonation by perchloric acid [1]. We now report preliminary results of a study on the coordinating properties of these compounds towards metals of the first transition series.

The reactions investigated are shown in Scheme 1. The α-diimino com-



* To whom correspondence should be addressed.

plex I reacts rapidly with anhydrous MCl_2 in a 10:1 v/v mixture of CH_2Cl_2/C_2H_5OH to give the adducts III, which can be recrystallized from the same solvent mixture (yields 70–80%). Satisfactory elemental analyses have been obtained for all products. Molecular weight measurements show that the bimetallic complexes III are monomeric in 1,2-dichloroethane solution. From the magnetic moment values (see Table 1) it appears that products IIIa–IIIe are paramagnetic high-spin complexes.

TABLE I
IR DATA AND MAGNETIC MOMENTS OF COMPOUNDS I–III

Compound	$\nu(C=N)$ (cm^{-1})	$\nu(Pd-Cl)$ (cm^{-1})	$\nu(M-Cl)$ (cm^{-1})	μ_{eff} (BM)
I	1616m 1550m	265m		
IIIa	1588mw	302m	358ms 327m	5.18
IIIb	1581mw	300m	350ms 333m	4.36
IIIc	1580mw	295m	340ms 330(sh)	3.24
IIId	1579mw	308(sh) or 297ms	329ms 308(sh) or 297ms	2.50
IIIe	1580(sh)	302m	337ms 325(sh)	

Only one $\nu(C=N)$ band of low intensity is observed upon coordination of the α -diimino group. This is probably due to a delocalised π -electron system being formed on the five-membered ring by interaction of the $C=N$ double bonds with the metal d orbital of appropriate symmetry [2,3]. This view is also supported by the down-field shift of the methyl signal, $\delta(C-Me)$, which occurs at 2.27 ppm in the 1H NMR spectrum of the zinc derivative IIIe, relative to the corresponding signals of the ligand I (1.29 ppm) and the protonated ligand II (1.51 ppm) [1]. As can be seen, the $\nu(Pd-Cl)$ band of the coordinated ligand is shifted by ca. 30–40 cm^{-1} to higher frequencies, a similar effect being observed also in the protonation product II [1].

Electronic spectra in the visible and near-infrared region indicate a tetrahedral configuration around the metal M both in the solid and in dichloromethane solution. For example, the spectrum of the cobalt adduct IIIb shows $d-d$ bands in the regions 590–700 nm and 1000–1700 nm, which are typical of tetrahedral or pseudotetrahedral $[CoCl_2 L_2]$ complexes [4].

For the copper complex IIId, however, a planar configuration cannot be ruled out, but a distorted tetrahedral structure is probably imposed by the steric requirements of the ligand [5].

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