

Preliminary communication

BINUCLEAR MIXED METAL CYCLOMETALLATED COMPLEXES

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Summary

The preparation of the first mixed metal cyclometallated compounds $[\text{ClPd}(p\text{-RC}_6\text{H}_3\text{CH}=\text{N}-\text{N}=\text{CH}(p\text{-RC}_6\text{H}_3))\text{PtCl}]_n$ ($\text{R} = \text{H}, \text{Cl}$) are reported; they were made from monocyclopalladated $[(\text{AcO})\text{Pd}(p\text{-RC}_6\text{H}_3\text{CH}=\text{N}-\text{N}=\text{CH}(p\text{-RC}_6\text{H}_4))_2$ and PtCl_4^{2-} .

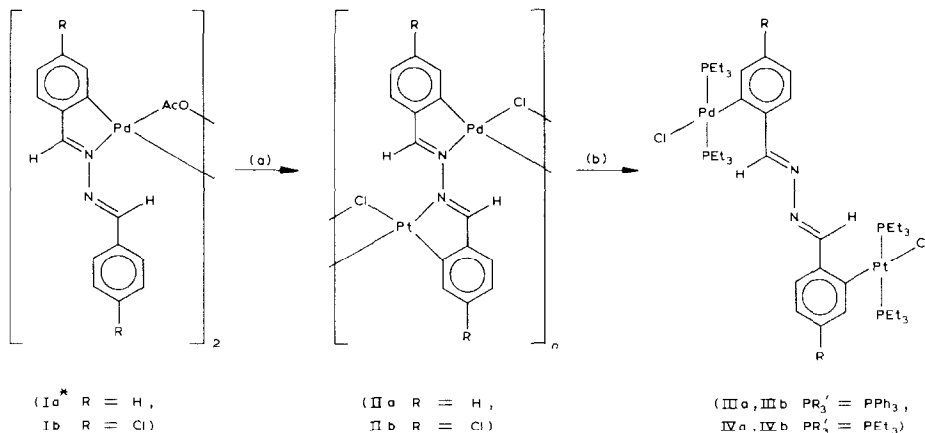
Cyclometallation reactions have attracted much attention in the last years. The complexes so formed have been used in regiospecific organic syntheses [1], as well as to prepare compounds with metal-metal bonds [2], and, more recently, binuclear hydrido-bridged complexes [3]. However, only a few binuclear cyclometallated compounds of N-donor ligands have been reported. To the best of our knowledge, palladium *N,N,N',N'*-tetraalkylxylenediamines [4], and azobenzene-nickel or -manganese [5,6] derivatives represent the only examples. No binuclear cyclometallated compounds with two different metals have been described; when $[\text{MnMe}(\text{CO})_5]$ is added to the monometallated compounds $[\text{Pd}(\text{C}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_5)(\text{C}_5\text{H}_5)]$ or $[\text{RhCl}(\text{C}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_5)]_2$, only ligand transfer takes place, giving $[\text{Mn}(\text{C}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_5)(\text{CO})_4]$ in good yield [6].

Recently, we described the reaction of PdCl_2 with benzalazines, which leads exclusively to the dicyclopalladated compounds $[\text{ClPd}(p\text{-RC}_6\text{H}_4\text{CH}=\text{N})]_n$ [7], but with $\text{Pd}(\text{AcO})_2$, either mono-, $[(\text{AcO})\text{Pd}(\text{C}_6\text{H}_4\text{CH}=\text{N}-\text{N}=\text{CHC}_6\text{H}_5)]$ [8], or dicyclopalladated compounds, $[(\text{AcO})\text{Pd}(p\text{-RC}_6\text{H}_3\text{CH}=\text{N})]_n$ [9] can be formed, depending on the conditions used. These results show that the dicyclopalladation takes place in two steps, and that the donor properties of one nitrogen of benzalazine are not seriously affected by coordination of the second nitrogen to a metal.

In continuation of our investigations of dimetallated azine compounds, we report here the preparation of the first mixed metal complexes by treatment of PtCl_4^{2-} with the monocyclopalladated complexes containing these ligands.

The cyclometallated dimeric compounds Ia and Ib, were obtained by refluxing a solution of $\text{Pd}(\text{AcO})_2$ and the azine (1/1) in anhydrous acetic acid for 30 min. The reaction of these compounds with a stoichiometric amount of

K_2PtCl_4 in refluxing anhydrous acetic acid for 24 h gives very insoluble precipitates of IIa and IIb, respectively. These polymeric species were then split with phosphines to give the monomeric species, IIIa, IIIb and IVa, IVb, for easier characterization. The corresponding reactions between the dimers Ia and Ib and $[MnMe(CO)_5]$ in refluxing heptane for 24 h led only to decomposition of the organometallic compounds.



SCHEME 1. (a) $Pd(AcO)_2$, $HAcO$ reflux, 30 min; (b) K_2PtCl_4 , $HAcO$ reflux, 24 h. * previously obtained by Heck and Thompson, see ref. 8.

Elemental analyses and IR spectra were found to be satisfactory. The proton NMR spectra (200 MHz) of IVa, IVb in $CDCl_3$ show two azomethine signals for each compound, at lower fields than those for the starting non-metallated azines. These downfield shifts are due to the paramagnetic anisotropy of the metal, and show the close vicinity of the two azomethine protons to the two different metals. The signals at lower fields, 9.53 ppm (IVa) and 9.48 ppm (IVb), are assigned to the azomethine protons near platinum, and that at upper fields, 9.35 ppm (IVa) and 9.31 ppm (IVb), to the azomethine protons near the palladium, in accord with the values observed in the dimetallated compounds, $[M(p-R-C_6H_3CH=N)Cl(PEt_3)_2]_2$, $M = Pd$ or Pt .

The ^{31}P - $\{^1H\}$ NMR spectra (80.98 MHz; $CDCl_3$; relative to H_3PO_4) show, one singlet at 13.29 ppm (IVa) or 13.26 ppm (IVb) and a pseudotriplet at 13.77 ppm, $^1J(Pt-P)$ 2716 Hz (IVa) or 13.58 ppm, $^1J(Pt-P)$ 2659 Hz (IVb), due to ^{195}Pt coupling, indicating a *trans* configuration of the PEt_3 ligands.

References

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