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Preliminary communication

SUBSTITUTION REACTIONS OF BINUCLEAR PALLADIUM(I) AND PLATINUM(I) ISOCYANIDE COMPLEXES

J.R. BOEHM and A.L. BALCH*
Department of Chemistry, University of California, Davis, California 95616 (U.S.A.)
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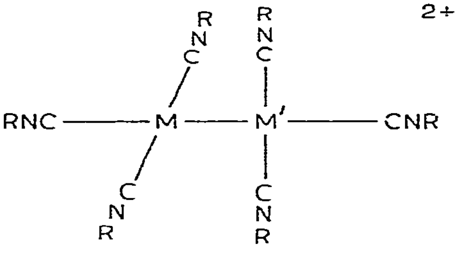
Summary

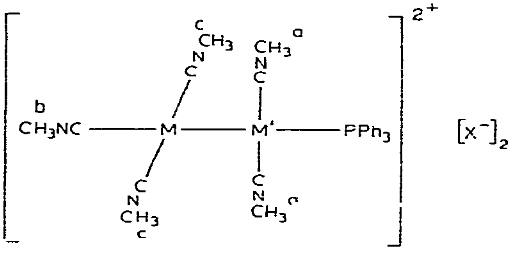
The palladium(I) and platinum(I) complexes $[(CH_3NC)_6M_2]^{2+}$ undergo substitution reactions with isocyanides, phosphines and halide or pseudohalide ions. With triphenylphosphine, axial substitution is preferred. The product $[(CH_3NC)_5(Ph_3P)Pd_2]^{2+}$ is fluxional.

Although the structures of several dimeric, metal—metal bonded palladium(I) and platinum(I) complexes are known [1], there is little information available about the chemical reactions of these dimers. Here are reported details of substitution reactions of the non-bridged dimers I—III which have been recently synthesized [2] and structurally characterized [3].

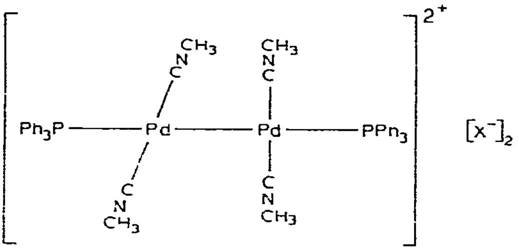


(I) M = M′ = Pd, R = CH_3
(II) M = M′ = Pt, R = CH_3
(III) M = Pd, M′ = Pt, R = CH_3

As might be anticipated for coordinatively unsaturated species, the dimers I, II and III readily undergo ligand exchange reactions. Ligand exchange between I or II and free methyl isocyanide is fast on a PMR time scale. Only a single, averaged methyl resonance is observed for acetone solutions of I or II and methyl isocyanide over the temperature range 40 to −50°C. The ease of substitution coupled with the ease of removal of displaced methyl isocyanide through volatilization has allowed the isolation of a number of substitution products. Treatment of I with an excess of t-butyl isocyanide results in the substitution of all isocyanide ligands: $[(t\text{-}C_4H_9NC)_6Pd_2](PF_6)_2$ (ν(C≡N) 2200 cm^{-1}) has been isolate from this reaction. Similarly $[(C_6H_5NC)_6Pd_2](PF_6)_2$ (ν(C≡N) 2190 cm^{-1}) has been isolated from the reaction of I with phenyl isocyanide. Complex I has been recovered unchanged after exposure to carbon monoxide, pyridine, 2,2'-bipyridine, and olefins, such as 1,5-cyclooctadiene and tetrachloroethylene. However phosphines, particularly triphenylphosphine, may be substituted for some of the isocyanide ligands in these complexes. Depending on the quantity of triphenylphosphine used either the monosubstituted products IV and V or the di-substituted products VI—VIII have been obtained. These products show isocyanide stretching vibrations characteristic of only terminal isocyanide ligands and presumably retain the basic geometry of I. It has not been possible to incorporate more than two triphenylphosphine ligands into these complexes, even when a large excess of this ligand was employed. In most cases the triphenylphosphine ligands occupy the axial coordination sites preferentially. Thus the PMR spectra of the di-substituted compounds VI, VII and VIII show methyl resonances due to equatorial isocyanide ligands only. In the case of the dipalladium species VI this single resonance is unsplit on cooling in acetone solution to –84°C.



(IV) $M = M' = Pd, X = PF_6^-$
(V) $M = M' = Pt, X = BF_4^-$



(VI) $M = M' = Pd, X = PF_6^-$
(VII) $M = M' = Pt, X = BF_4^-$
(VIII) $M = Pd, M' = Pt, X = PF_6^-$

In addition to establishing the geometry of IV, the PMR spectrum of IV indicates that this complex, like I, is fluxional. The PMR spectrum of IV in acetone solution below –8°C consists of three methyl resonances at τ 6.54, 6.37 and 6.29 ppm (relative intensities; 2:1:2) which are assigned to groups a, b, and c respectively. Above –8°C the resonances at 6.29 and 6.37 broaden, coalesce at –3°C, and narrow on further heating. During these changes, the resonance at 6.54 ppm remains unperturbed. Heating IV to +40°C does not alter the spectrum any further. Upon cooling, the PMR spectral changes are reversed. The temperature dependence of the PMR spectrum of IV (M = M' = Pd) is not affected by changes in the concentration of IV or by adding palladium chloride to scavange free methyl isocyanide. Consequently the fluxional process of IV, like that of I, is intra-ionic. Since all of the isocyanide ligands in IV do not become equivalent during the fluxional process, a mechanism involving bridging isocyanide ligands does not appear reasonable for this process. Rather a process creating tetrahedral geometry at palladium and allowing free rotation about the Pd—Pd bond would be sufficient to account for the observations. The methyl region of the PMR spectrum of V is broad and complex; a thorough analysis has been thwarted by the lack of resolution. Since the spectrum is more complex than would be expected even when extensive coupling to ^{195}Pt is considered, it appears that both axial and equatorial substitution may have occurred in V.

Complex I also undergoes substitution reactions with anions. Addition of potassium thiocyanate or sodium iodide to I in acetonitrile solution results in the formation of the neutral complexes $Pd_2(SCN)_2(CNCH_3)_4$ (ν(CN) 2219 cm^{-1}; ν(CNS) 2094 cm^{-1}) and $Pd_2I_2(CNCH_3)_4$ (ν(CN) 2212 cm^{-1}). Similarly $Pd_2(CNC_6H_5)_6{}^{2+}$ is converted into $Pd_2I_2(CNC_6H_5)_4$ and $Pd_2(CN\text{-}t\text{-}C_4H_9)_6{}^{2+}$ into $Pd_2I_2(CN\text{-}t\text{-}C_4H_9)_4$, a complex which has been previously prepared by two different routes [4]. These metal complexes probably have planar structures with bridging anions and direct Pd—Pd bonds.

Acknowledgement

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References

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