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Preliminary communication

NEW BIMETALLIC ORGANOPALLADIUM(II) COMPOUNDS CONTAINING A Pd—Co OR Pd—Mo BOND *trans* TO A Pd—C BOND

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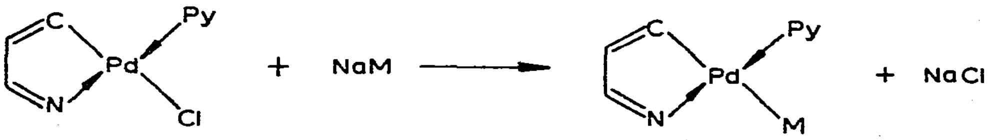
Summary

The reaction of a chelated palladium compound with $Co(CO)_4^-$ and $[Mo(CO)_3\text{-}\eta\text{-}C_5H_5]^-$ gives new stable bimetallic Pd—Co and Pd—Mo complexes in which the metal—metal bond is *trans* with respect to the Pd—carbon σ-bond.

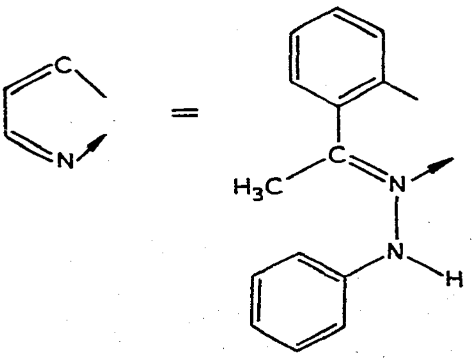
There is much interest in compounds containing metal—metal bonds [1], but little work has been done on palladium—transition metal derivatives [2—4]. Those which have been studied involve trimetallic chains of the type M—Pd—M



(1)

(I)

(IIa) M = $Co(CO)_4^-$
(IIb) M = $[Mo(CO)_3\text{-}\eta\text{-}C_5H_5]^-$
(IIc) M = $Mn(CO)_5^-$
(IId) M = $[Fe(CO)_2\text{-}\eta\text{-}C_5H_5]^-$



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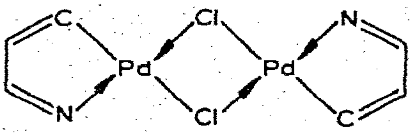
(M = Mn, Co, Mo) [2] or bridged species [3, 4], and no stable bimetallic compounds in which a Pd—transition metal bond alone connects the two halves of the molecule, have been reported.

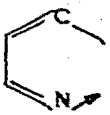
We describe below the isolation of the first compounds containing bimetallic Pd—Co and Pd—Mo bonds, and attempts to make similar Pd—Mn and Pd—Fe derivatives. The reaction used is shown in eqn. 1. Compound I was obtained by the bridge-cleaving reaction of



[5]

with pyridine, and is known to have the Cl atom *trans* to the σ-bonded carbon atom [6].

Solutions of NaM [M = $Co(CO)_4^-$, $(Mo(CO)_3\text{-}\eta\text{-}C_5H_5)^-$] reacted at −10°C under purified N_2 with a suspension of I in THF to form IIa and IIb. The products were recrystallized from THF/pentane, and gave satisfactory elemental analyses. The crystals are air stable for many days in the case of IIa and for some hours in the case of IIb. Their THF solutions are stable for many hours at room temperature under N_2. This behaviour is in marked contrast to the instability of *trans*-$PdPy_2[Co(CO)_4]_2$ (III) [2c] and *trans*-$PdPy_2[Mo(CO)_3\text{-}\eta\text{-}C_5H_5]_2$ (IV) [2b]. The fairly high stability may be due to (i) replacement of a relatively labile M group (in III and IV with M—Pd—M) by a non-labile σ-bonded carbon (in IIa and IIb with C—Pd—M), and (ii) to the stabilizing effect of the chelate ring



in the cyclic palladium compounds.

The high *trans* influence of the σ-bonded C (cf. ν(Pd—Cl) 271 cm^{-1} in IR of I) makes the M group even more anionic than in III and IV, as shown by the lower ν(CO) IR frequencies: (IIa) 2022 s, 1942 s, 1883 s (KBr); 2027 s, 1946 s, 1885 s (THF). (III) 2018 s, 1965 s, 1915 s (KBr); 2020 s, 1975 m, 1918 w (THF). (IIb) 1910 s, 1812 s, 1775 s (KBr). (IV) 1954 m, 1891 s, 1832 s, 1803 s (KBr). From the mean ν(CO) frequencies, the negative charge left on M is estimated at ca. 0.7 electron in IIa as opposed to 0.55 in III [2d].

With M = $Mn(CO)_5^-$ in reaction 1, the solution product decomposes above −20°C, and compound IIc could not be obtained as a solid. With M = $[Fe(CO)_2\text{-}\eta\text{-}C_5H_5]^-$ the solution decomposed immediately even at −80°C. We therefore suggest the following order of stability for the bimetallic Pd—M species: M = $Co(CO)_4^- > [Mo(CO)_3\text{-}\eta\text{-}C_5H_5]^- \gg Mn(CO)_5^- > [Fe(CO)_2\text{-}\eta\text{-}C_5H_5]^-$. This parallels the order of increasing nucleophilicities of the carbonylmetallate anions [7]. Although $[Mo(CO)_3\text{-}\eta\text{-}C_5H_5]^-$ and $Mn(CO)_5^-$ are not very different in nucleophilicity, the latter has the disadvantage of being more bulky.

The above trend would also be consistent with an antisymbiotic effect at the Pd^{II} center [8], in which the soft σ-bonded C prefers a relatively weak nucleophile [$Co(CO)_4^-$] in the *trans* position or in which the bond to the soft group [$Fe(CO)_2$-η-C_5H_5]$^-$ is weakened when *trans* to carbon. Further experiments are in progress in connection with these possibilities.

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