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NEW COMPOUNDS CONTAINING Pt–Mo AND Pd–Mo BONDS

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SUMMARY

The preparation and properties of three new compounds *trans*-$PtPy_2Cl[\pi\text{-}C_5H_5Mo(CO)_3]$, *trans*-$PtPy_2[\pi\text{-}C_5H_5Mo(CO)_3]_2$ and *trans*-$PdPy_2[\pi\text{-}C_5H_5Mo(CO)_3]_2$ are described. The last two compounds have the same crystal structure, as is shown by their powder diagrams. The infrared spectra in KBr and Nujol reveal 4 bands in the region characteristic of the CO stretching mode and the similarities of these spectra are stressed.

INTRODUCTION

Many organometallic compounds with metal–metal bonds are now known[1–2]. In connection with our study of metal–metal bonded complexes involving 4-coordinate d^8 transition metal ions[3,4] it was of interest to take as substrate *trans*-PtL_2Cl_2 or *trans*-PdL_2Cl_2 and observe the influence of L on the stability of the metal–metal bond obtained by reaction with the anion of a metal carbonyl or substituted metal carbonyl anion.

RESULTS AND DISCUSSION

Previously we described[4] the preparation and properties of compounds with Pt–Co and Pt–Mn bonds. We now report the preparation and some properties of two new compounds, (I) and (II), containing Pt–Mo bonds and of a new compound, (III), containing a Pd–Mo bond. The reactions are:

$$2\ \textit{trans}\text{-}PtPy_2Cl_2 + 3\ Na[\pi\text{-}C_5H_5Mo(CO)_3] \rightarrow$$
$$3\ NaCl + \underset{\text{(I)}}{\textit{trans}\text{-}PtPy_2Cl[\pi\text{-}C_5H_5Mo(CO)_3]} + \underset{\text{(II)}}{\textit{trans}\text{-}PtPy_2[\pi\text{-}C_5H_5Mo(CO)_3]_2} \quad (1)$$

$$\textit{trans}\text{-}PdPy_2Cl_2 + 2\ Na[\pi\text{-}C_5H_5Mo(CO)_3] \rightarrow$$
$$2\ NaCl + \underset{\text{(III)}}{\textit{trans}\text{-}PdPy_2[\pi\text{-}C_5H_5Mo(CO)_3]_2} \quad (2)$$

The platinum compounds are stable in air but decompose slowly in tetrahydrofuran (THF). The palladium compound decomposes slowly in air and very rapidly in solution. Products (II) and (III) give the same powder diagrams, which is in accord with the similarity in the covalent radii of Pt and Pd. Close similarity of the IR spectra in the carbonyl stretching region is also observed. Two points are of particular interest: both for Nujol mulls (Table 2) and KBr pellets we observed four bands for (I), (II) and (III). In solution in THF or $CHCl_3$ only three bands are observed, for compounds (I) and (II) as expected for a C_s local symmetry ($2A'+A''$); (I): 1920 m, 1890 s, 1820 s; (II): 1910 m, 1890 s, 1820 s. The band at 1820 cm^{-1} may be attributed to the CO stretching mode (A') in-plane with respect to the symmetry plane C_s and *trans* with respect to the Pt–Mo bond. The band at 1960 cm^{-1} is displaced toward lower frequencies in THF solution, probably owing to a solvent effect. The fact that the mode at 1820 cm^{-1} in solution is split (1820, 1794 cm^{-1}) in the crystal could be explained by steric hindrance between two molecules in the unit cell, although the data are insufficient to permit definite conclusions. Alternatively splitting may be due to the mode of dispersion in Nujol.

It is noteworthy that the CO stretching frequencies of the two *trans*-$PtPy_2Cl[\pi\text{-}C_5H_5Mo(CO)_3]$ and *trans*-$PtPy_2[\pi\text{-}C_5H_5Mo(CO)_3]_2$ in solution are very similar. These three bands are comparable with those reported by Haines, Nyholm and Stiddard[5] for $\pi\text{-}C_5H_5(CO)_3Mo\text{–}AuL$, and are consistent with the soft character of the Pt^{II} center.

On the other hand, the Pt–Cl stretching frequency of (I) appears at 348 cm^{-1},

TABLE 1

PHYSICAL CHEMICAL PROPERTIES AND ANALYTICAL DATA

Compound	Color	Decompn. temp. (°C)	Yield (%)	Solubility (mg/ml)		Analysis found (calcd.) (			
				THF	$CHCl_3$	C	H	N	M[a]
trans-$PtPy_2Cl_2$	Yellow	256				27.6 (28.3)	2.4 (2.4)	6.7 (6.6)	45. (46.
trans-$PtPyCl[\pi\text{-}C_5H_5Mo(CO)_3]$	Orange	186–188	48	0.6	0.3	33.6 (34.2)	2.4 (2.4)	4.5 (4.4)	30. (30.
trans-$PtPy_2[\pi\text{-}C_5H_5Mo(CO)_3]_2$	Red	188–190	23	0.7	0.3	35.8 (37.0)	2.3 (2.4)	3.3 (3.3)	22. (23.
trans-$PdPy_2[\pi\text{-}C_5H_5Mo(CO)_3]_2$	Dark-violet	80–85	57	2.8	2.4	40.3 (41.4)	2.7 (2.6)	3.6 (3.7)	14. (14.

[a] M = Pt or Pd.

TABLE 2

IR FREQUENCIES (cm^{-1})

Compound	CO Stretching[a]	Other vibrations	ν(Pt–Cl)
trans-$PtPy_2Cl_2$		480m	342m
trans-$PtPy_2Cl[\pi\text{-}C_5H_5Mo(CO)_3]$	1960m 1893s 1820s 1800s	608m 570s 510s 487m	348m
trans-$PtPy_2[\pi\text{-}C_5H_5Mo(CO)_3]_2$	1960m 1892s 1820s 1794s	602m 565s 505m 480m	
trans-$PdPy_2[\pi\text{-}C_5H_5Mo(CO)_3]_2$	1954m 1891s 1832s 1803s	600m 568s 505s 480m	

[a] The CO stretching frequencies were measured in Nujol for (III), other bands in KBr pellet.

which compares with 342 cm^{-1} in *trans*-$PtPy_2Cl_2$ as previously reported[6,7], and confirmed by us. This displacement may indicate a greater strength of the Pt–Cl bond and a moderate *trans* labilizing effect[8] of $[\pi\text{-}C_5H_5Mo(CO)_3]^-$, which explains the formation of both the compounds (I) and (II) from reaction (1).

A definite assignment of Pt–Mo and Pd–Mo frequencies has not yet been made and will be published later.

EXPERIMENTAL

The reactions were carried out under dry nitrogen in THF distilled from sodium/benzophenone. Commercially available $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ (Alpha Inorganic Chemicals, Inc.) was employed. *Trans*-$PtPy_2Cl_2$ and *trans*-$PdPy_2Cl_2$ were prepared respectively by the methods of Kauffman[9] and Krauss and Brodkorb[10]. Solutions of $Na[C_5H_5Mo(CO)_3]$ were prepared by reduction with Hg/Na[11] of a THF solution of $[\pi\text{-}C_5H_5Mo(CO)_3]_2$.

Microanalyses for C, H, N (Table 1) were performed in our Institute (those of *trans*-$PtPy_2Cl_2$ are given for comparison). Platinum was determined by the stannous chloride colorimetric method[12] and palladium by the *p*-nitrosodimethylaniline colorimetric prodecure[13]. IR spectra (Table 2) were obtained using a Beckman Spectrophotometer Model IR 12.

Preparation of trans-$PtPy_2Cl[\pi\text{-}C_5H_5Mo(CO)_3]$ and trans-$PtPy_2[\pi\text{-}C_5H_5Mo(CO)_3]_2$

120 ml of a solution of $Na[\pi\text{-}C_5H_5Mo(CO)_3]$ in THF prepared from 3.7 mmoles of $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ were added to 3.3 mmoles of *trans*-$PtPy_2Cl_2$ in approximately 200 ml of THF. The mixture was stirred and heated for 30 h under reflux. The *trans*-$PtPy_2Cl_2$ reacted and dissolved slowly with formation of a red product. Recrystallization from dichloromethane/pentane afforded the *trans*-chloro-(π-cyclopentadienyltricarbonylmolybdato)bis(pyridine)platinum(II) (Product I) and the *trans*-bis(π-cyclopentadienyltricarbonylmolybdato)bis(pyridine)platinum(II) (Product II).

Preparation of trans-$PdPy_2[\pi\text{-}C_5H_5Mo(CO)_3]_2$

The reaction was carried out as above but at a lower temperature (approximately −30°). As expected, the reaction was very fast and the product was destroyed in THF solution at room temperature. We obtained the *trans*-bis(π-cyclopentadienyltricarbonylmolybdato)bis(pyridine)palladium(II) (Product III).

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