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trans-BIS(TETRACARBONYLCOBALTATO)BIS(PYRIDINE)PLATINUM(II) AND *trans*-BIS(PENTACARBONYLMANGANATO)BIS(PYRIDINE)-PLATINUM(II)

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SUMMARY

The preparation and properties of *trans*-$PtPy_2[Co(CO)_4]_2$ and *trans*-$PtPy_2[Mn(CO)_5]_2$ are described. The metal carbonyl anion $Co(CO)_4^-$ is studied as a leaving group by measuring the rate of the cleavage reactions

$$PtPy_2[Co(CO)_4]_2+2\,Y \rightleftarrows [PtPy_2Y_2]^{2+}+2\,Co(CO)_4^-$$

$Y=(C_6H_5)_3P$, $(n\text{-}C_4H_9)_3P$ in tetrahydrofuran. The products of these reactions are also described.

INTRODUCTION

Many organometallic compounds with metal–metal bonds are now known[1,2]. Most of them are prepared by nucleophilic attack of a metal carbonyl anion on a substrate which contains a metal of group IVb[3–5], IIIb[6], IIb[5,7] and Ib[8]. It was of interest to generalize the preparation of compounds with metal–metal bonds in using other substrates containing transition elements. We have taken the substrate *trans*-$PtPy_2Cl_2$ because it allowed us to use the metal carbonyl anion nucleophilicities studied by Dessy[9] and the susceptibility towards nucleophilic attack studied for *trans*-$PtPy_2Cl_2$[10]. The new metal–metal bonding may be compared with that in $(CO)_5Mn$–$Re(CO)_5$ or $Cp(CO)_2Fe$–$Mo(CO)_3Cp$[11]. The study of $Co(CO)_4^-$ as a leaving group in the reaction

$$trans\text{-}PtPy_2[Co(CO)_4]_2+Y^- \rightleftarrows trans\text{-}[PtPy_2Y_2]^{2+}+2\,Co(CO)_4^-$$

gave, with neutral molecules such as $Y=PPh_3$, $P(n\text{-}C_4H_9)_3$ the *trans*-$PtPy_2Y_2$-$[Co(CO)_4]_2$ compounds which are also described.

EXPERIMENTAL SECTION

All reactions and crystallizations were carried out under a nitrogen atmosphere, mainly by the use of Schlenk tube techniques. Tetrahydrofuran (THF) was purified by distillation from lithium aluminum hydride under nitrogen just

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before the preparation. $Mn_2(CO)_{10}$ and $Co_2(CO)_8$ were commercially available (Alpha Inorganic Chemicals, Inc.). *Trans*-$PtPy_2Cl_2$ was prepared according to the method of Kauffman[12]. The reagent $(C_6H_5)_3P$ was recrystallized twice from methanol. Tri-n-butylphosphine was distilled under nitrogen before use. Reactions were carried out in general accordance with Gorsich's procedures[13] where $NaMn(CO)_5$ and $NaCo(CO)_4$ were used but not isolated. Solutions of $NaCo(CO)_4$ and $NaMn(CO)_5$ were prepared by reduction of a THF solution of dicobalt octacarbonyl and dimanganese decacarbonyl with a slight excess of 1% sodium amalgam.

TABLE 1

PHYSICAL CHEMICAL PROPERTIES AND ANALYTICAL DATA

Compound	Color	Decompn. temp. (°C)	Yield (%)	Analysis (%)					
				Carbon		Hydrogen		Nitrogen	
				Calcd.	Found	Calcd.	Found	Calcd.	found
trans-$PtPy_2[Mn(CO)_5]_2$[a]	Orange-red	160–162	54	32.32	31.93	1.36	1.05	3.77	3.62
trans-$PtPy_2[Co(CO)_4]_2$	Red-brown	152–155	65	31.10	31.23	1.45	1.32	4.09	3.93
trans-$PtPy_2(PPh_3)_2[Co(CO)_4]_2$	Yellow	136–138	47	53.17	53.0	3.30	3.28	2.30	2.45
trans-$PtPy_2[P(n\text{-}C_4H_9)_3]_2$-$[Co(CO)_4]_2$	Yellow		56	45.86	45.41	5.86	5.79	2.55	2.47

[a] Found: Mn, 14.54; Pt, 25.85; calcd.: Mn, 14.78; Pt, 26.25%; solubility: the *trans*-$PtPy_2[Co(CO)_4]_2$ is more soluble in THF (5 mg/ml) and in CH_2Cl_2 (10 mg/ml) than is *trans*-$PtPy_2[Mn(CO)_5]_2$, 2mg/ml in THF and 2 mg/ml in CH_2Cl_2. Both are little soluble in cyclohexane or pentane.

Microanalyses for C, H, N (Table 1) were performed in our Department by Miss H. Beck. Platinum was determined by the stannous chloride colorimetric method[14a] and manganese as permanganate by a periodate method[14b].

IR spectra (Table 2) were obtained using a Perkin–Elmer Model 337 grating spectrometer equipped with a Servo Rite expanded scale recorder. Dichloromethane or THF were used as solvents because of the low solubility of the products in cyclohexane and their instability in methanol. Kinetic measurements on *trans*-$PtPy_2$-$[Co(CO)_4]_2$ were carried out in THF by observing the rate of disappearance of the highest energy CO stretching band at 2025 cm^{-1}. Pseudo first-order conditions, using at least a twenty-fold excess of reagent were realized. With tri-n-butylphosphine a semi-flow technique was used.

One hundred ml of a solution 10^{-3} *M* in *trans*-$PtPy_2[Co(CO)_4]_2$ was stirred (magnetically) in a 200 ml flask; tri-n-butylphosphine was introduced at the time $t = 0$ with a syringe. Every minute about 4–5 cc of the solution was withdrawn with a syringe, passed through the cell, and discarded with another syringe. The transmittance was recorded during the flow on the recorder. The value was taken when it had stabilized.

Triphenylphosphine was added in the solid state to a solution 10^{-3} *M* in *trans*-$PtPy_2[Co(CO)_4]_2$ prepared just before the experiment, in a volumetric flask closed with a "sleeve-type" rubber stopper. Samples were withdrawn at intervals and their spectra recorded in 1 mm NaCl cells.

Preparation of trans-$PtPy_2[Co(CO)_4]_2$

Two g (5 mmoles) of solid *trans*-$PtPy_2Cl_2$ was added to approximately 200 ml

TABLE 2

IR FREQUENCIES (CM^{-1})

Compound	CO stretching			Other vibrations			
trans-PtPy$_2$[Mn(CO)$_5$]$_2$ [a]	2035 s	1960 s	1920 s	578 m	552 vw	505 m	478 m
	[$A_1^{(2)}$]	[B_1]	[$A_1^{(1)}E$]	452 s	420 s	438 m	
trans-PtPy$_2$[Co(CO)$_4$]$_2$	2025 s	1975 s	1900 sh	560 s	530 s	490 m	470 s 420 m
trans-PtPy$_2$(PPh$_3$)$_2$[Co(CO)$_4$]$_2$	2005 w	1878 sb		552 (sh)	540 s	522 (sh)	495 w
trans-PtPy$_2$(PPh$_3$)$_2$(tosylate)$_2$				560 m	540 m	520 s	510 (sh)
trans-PtPy$_2$[P(C$_4$H$_9$)$_3$]$_2$[Co(CO)$_4$]$_2$	2003 w	1902 (sh)	1888 s 1874 (sh)		550 s		
Co(CO)$_4^-$			1883 vs	555 vs			

[a] The CO stretching frequencies were measured in THF; other bands in KBr pellet. Assignments as Graham *et al.* (ref. 4). The force constants k_1, k_2, k_i, as defined by F. A. Cotton and C. S. Kraihanzel (ref. 15); k_1 = 14.89 md/Å; k_2 = 15.502 md/Å; k_i = 0.306. These give a calculated frequency for the B_1 band of 1959 cm^{-1}.

of a stirred solution of Na[Co(CO)$_4$] prepared from 2.1 g (6 mmoles) of $Co_2(CO)_8$ and heated for 4 h under reflux and a nitrogen atmosphere. The *trans*-PtPy$_2$Cl$_2$ reacted and dissolved slowly. After filtration, THF was removed at reduced pressure. Two recrystallizations from dichloromethane/pentane afforded the red-brown pure product which is stable in air for two or three weeks but is decomposed in methanol or THF solution, even with the exclusion of air.

Preparation of trans-PtPy$_2$[Mn(CO)$_5$]$_2$

The preparation is the same as above and gives a red-orange product which is again stable in air but not in solution.

Preparation of trans-PtPy$_2$(PPh$_3$)$_2$[Co(CO)$_4$]$_2$

Triphenylphosphine (276 mg, 1.05 mmole) in 50 ml of THF was added at room temperature to a stirred solution of 247.6 mg (0.5 mmole) of *trans*-PtPy$_2$-[Co(CO)$_4$]$_2$ in 80 ml of THF. A yellow product precipitated; after a half hour it was filtered, washed with dichloromethane and recrystallized from acetonitrile.

Preparation of trans-PtPy$_2$[(n-C$_4$H$_9$)$_3$P)$_2$[Co(CO)$_4$]$_2$

Tributylphosphine (205 mg, 1.02 mmole) was added at room temperature to 348 mg (0.5 mmole) of *trans*-PtPy$_2$[Co(CO)$_4$]$_2$ in 100 ml of THF. The solution became yellow at once. After one-half hour the THF was removed under reduced pressure. The produce was recrystallized from dichloromethane/pentane.

DISCUSSION

The two compounds *trans*-PtPy$_2$[Co(CO)$_4$]$_2$ and *trans*-PtPy$_2$[Mn(CO)$_5$]$_2$ are new and reported here for the first time. The *trans* structure of both compounds has been established by single crystal X-ray diffraction studies[17]. Physical properties and analytical data are reported in Table 1. The compounds are stable in air but not in solution. In methanol, in following the disappearance of the CO stretching bands at 1980 cm^{-1} for *trans*-PtPy$_2$[Co(CO)$_4$]$_2$ [CO stretching bands at 2025 w, 1980 s, 1900 (sh) in methanol] we found a half-life for disappearance of one h at 25°, while in THF decomposition was about 50 times slower.

Three IR active carbonyl stretching modes (Table 2) are observed in THF or dichloromethane as expected with an effective symmetry C_{3v} about the Co or C_{4v} about the Mn atoms[2-4]. This means only a weak interaction exists between the two groups Co(CO)$_4$ or Mn(CO)$_5$ bound together through Pt. The actual symmetry is, of course, lower for both molecules. Thus for *trans*-PtPy$_2$[Mn(CO)$_5$]$_2$ we assign the band at 2035 cm^{-1} as $A_1^{(2)}$ at 1960 cm^{-1} as B_1 (inactive in C_{4v} symmetry) and $A_1^{(1)}$ and E both at 1920 cm^{-1}. This follows the suggestions of Cotton and Kraihanzel[15]. Using their equations we also calculate the force constants given in Table 2.

The two compounds *trans*-PtPy$_2$(PPh$_3$)$_2$[Co(CO)$_4$]$_2$ and PtPy$_2$[(n-C$_4$H$_9$)$_3$-P]$_2$[Co(CO)$_4$]$_2$ merit some discussion. Indeed it is possible that nucleophiles such as PPh$_3$ or (n-C$_4$H$_9$)$_3$P would attack the metal atom giving a substitution product such as *trans*-PtPy$_2$[Co(CO)$_3$Y]$_2$, or an insertion product such as[16] PtPy$_2$-[COCo(CO)$_3$Y]$_2$, but at no time was the appearance of a carbonyl band near 1620 cm^{-1} observed. Furthermore, the product of the triphenylphosphine reaction has an

TABLE 3

PSEUDO FIRST ORDER RATE CONSTANTS FOR THE REACTION *trans*-$PtPy_2[Co(CO)_4]_2 + (n\text{-}C_4H_9)_3P \rightarrow$ *trans*-$PtPy_2[(n\text{-}C_4H_9)_3P]_2[Co(CO)_4]_2$ IN THF AT 25°[a]

$(n\text{-}C_4H_9)_3P$ (M)	k_{obs} (sec^{-1})
0.038	4.47×10^{-4}
0.048	7.55×10^{-4}
0.068	8.9×10^{-4}
0.087	10.6×10^{-4}
0.152	21.0×10^{-4}

[a] The concentration of *trans*-$PtPy_2[Co(CO)_4]_2$ was 10^{-3} M.

IR spectrum and is similar to that *trans*-$PtPy_2(PPh_3)_2(tosylate)_2$[10]. The physical properties and analytical data are given in Table 1 and the IR data in Table 2.

The kinetic data of reaction (1) in THF with Y = tri-n-butylphosphine are reported in Table 3. A plot of k_{obs} *vs.* [Y] gives a straight line with a zero intercept and a slope of $k_2 = 1.25 \times 10^{-1}$ $M^{-1} \cdot sec^{-1}$. The pseudo first-order rate constants were obtained by following the disappearance of the CO stretching band at 2025 cm^{-1}. With triphenylphosphine the reaction goes more slowly and some destruction of the complex occurs. It was not possible to obtain good kinetic results, but k_2 appears to be about twenty times smaller than for the tributylphosphine. With pyridine as a nucleophile the reaction is slower still, and the complex decomposes before reaction occurs. The displacement reactions of *trans*-$PtPy_2[Mn(CO)_5]_2$ with nucleophiles also were too slow to be studied. It is expected that $Co(CO)_4^-$ will be a better leaving group than $Mn(CO)_5^-$, since it is a much weaker base. Compared with the chloride ion in *trans*-$PtPy_2Cl_2$, the cobaltcarbonylate anion has about equal leaving group ability[10]. It may also be noted that Dessy *et al.*[9] found $Mn(CO)_5^-$ to be a much better nucleophile than $Co(CO)_4^-$ towards methyl iodide. This also agrees with the relative leaving group abilities found in this work.

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REFERENCES

1 R. B. King, *Advan. Organometal. Chem.*, 2 (1964) 244.
2 T. H. Manuel, *Advan. Organometal. Chem.*, 3 (1965) 250.
3 D. J. Patmore and W. A. Graham, *Inorg. Chem.*, 5 (1966) 1406, 222.
4 W. Jetz, P. B. Simons, J. A. J. Thompson and W. A. Graham, *Inorg. Chem.*, 5 (1966) 2217.
5 M. Bigorgne and F. Benard, *Rev. Chim. Mineral.*, 3 (1966) 831.
6 W. Hieber and U. Teller, *Z. Anorg. Allg. Chem.*, 249 (1942) 43.
7 W. Hieber and R. Breu, *Chem. Ber.*, 90 (1957) 1259.
8 C. E. Coffey, J. Lewis and R. S. Nyholm, *J. Chem. Soc.*, (1964) 741.
9 R. E. Dessy, R. L. Pohl and R. D. King, *J. Amer. Chem. Soc.*, 88 (1966) 5121.
10 R. G. Pearson, H. Sobel and J. Songstad, *J. Amer. Chem. Soc.*, 90 (1968) 319.

11 R. B. King, P. M. Treichel and F. G. A. Stone, *Chem. Ind. (London)*, (1961) 747; A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova and I. Kolomnikov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, (1963) 194.
12 G. B. Kauffman, *Inorg. Syn.*, 7 (1963) 251.
13 R. D. Gorsich, *J. Amer. Chem. Soc.*, 84 (1962) 2486.
14 (a) E. B. Sandel, *Colometric Determination of Traces of Metals*, Interscience, New York, 3rd ed., 1959, p. 726; (b) p. 608.
15 F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, 84 (1962) 4432.
16 F. Basolo and R. G. Pearson, *Mechanism of Inorganic Reactions*, Wiley, New York, 1968, Chapt. VII.
17 R. Weiss and M. Moras, to be published.