occupies about the same position as ammonia in the spectrochemical series.

The effect of added pyrazole on the solution spectra of $NiPz_4Cl_2$ and $NiPz_6(BF_4)_2$ and the observed deviations from Beer's law indicate that some dissociation of the complex occurs even in acetonitrile solutions.

This study does not allow much to be said concerning the manner in which pyrazole is bound to the metal ion. The observed coordination numbers make π bonding appear to be unlikely. A more likely possibility is that bonding is through the "pyridine nitrogen," as is suggested for imidazole complexes.[8]

Acknowledgment.—The support of an American Cancer Society institutional grant is gratefully acknowledged.

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Replacement of Carbon Monoxide on Monosubstituted Molybdenum Carbonyl Derivatives

By Franco Zingales, Felice Faraone, Paolo Uguagliati, and Umberto Belluco

Even though a great amount of work has been done in the past year on substitution reactions of derivatives of the group VI and VII metal carbonyls, scant information is available concerning a systematic investigation of the *cis* effect in such reactions. On the ground of mainly preparative and infrared spectral observations, this effect was hitherto believed to be of rather minor importance inasmuch as two groups in *cis* positions are unable to compete for d electrons of the metal on as favorable terms as they do when in *trans* positions. As for the kinetic behavior of these systems, no appreciable *cis* effect appeared to be operative in the reactions of *cis*-CO dissociation from *cis*-$Mn(CO)_4$-$BrAs(C_6H_5)_3$ and from $Mn(CO)_5Br$.[1] An unusual detectable *cis* effect was displayed by the reactions of $M(CO)_4BrL$ with L' to give *cis*-$M(CO)_3BrLL'$ (M = Mn, Re). For instance, the rate constants for the dissociative path of the manganese complex at 40° range from 3.1×10^{-5} sec^{-1} for L = $P(OC_4H_9)_3$ to 77×10^{-5} sec^{-1} for L = $P(C_6H_5)_3$.[1] For the analogous reactions of rhenium compounds, the dissociative rate constants vary from 2.9×10^{-5} sec^{-1} for $P(n$-$C_4H_9)_3$ to 14×10^{-5} sec^{-1} for $P(C_6H_5)_3$ up to 87×10^{-5} sec^{-1} for γ-picoline.[2] Where the donor atom of the coordinated ligand L is the same (*e.g.*, phosphorus), mainly steric properties

of L have been invoked to account for this unprecedented *cis* effect. In order to throw some light on the factors by which a *cis* effect, if any, is governed, we have investigated the replacement of CO in monosubstituted molybdenym carbonyl derivatives of the type $Mo(CO)_5L$, by different neutral entering groups L' leading to *cis*-$Mo(CO)_4LL'$. The ligands L have been so chosen as to have about the same steric requirements, yet different σ-donor abilities.

Experimental Section

Preparation and Purification of Materials.—Pyridine, 4-picoline, 3-chloropyridine, and 3,4-lutidine (British Drug Houses) were distilled before use. Triphenylphosphine, triphenylarsine, and triphenylstibine, commercial reagent grade, were recrystallized from petroleum ether (bp 40–70°). Toluene (Analar, British Drug Houses) was refluxed over sodium wire and fractionally distilled before use in the kinetic studies.

The compounds $Mo(CO)_5L$ and *cis*-$Mo(CO)_4L_2$ (L = $P(C_6H_5)_3$, $As(C_6H_5)_3$, $Sb(C_6H_5)_3$) were prepared following the methods given in the literature.[3,4] The compounds $Mo(CO)_5L$ (L = pyridine, 4-picoline) were prepared by refluxing $Mo(CO)_6$ and a slight molar excess of the pyridine in a mixture of *n*-heptane and *n*-pentane boiling at 65°, under a nitrogen atmosphere for 6 hr. Under vacuum the solution was evaporated to dryness. The residue was washed with portions of pentane and the washings were cooled to −80°. The green-yellow crystals were filtered and dried. Excess $Mo(CO)_6$ was sublimed off at 50° under vacuum. The compounds *cis*-$Mo(CO)_4L_2$ (L = pyridine, 4-picoline) were prepared according to Kraihanzel and Cotton.[5]

The identity and purity of all of these compounds were confirmed by their carbon, hydrogen, and nitrogen analyses and by their infrared spectra.

Kinetic Studies.—All of the reactions were carried out by using an excess of the entering group in order to assure pseudo-first-order conditions. The reactions were followed by monitoring the disappearance of the highest frequency carbonyl stretching band of the starting material (*ca.* 3×10^{-3}–2×10^{-2} M). Measurements were taken over about 2 half-lives, since in all of the reactions an equilibrium was reached. However, the A_∞ value was taken as that of the base line, corresponding to the theoretically complete disappearance of the band. To make sure that in any case the *cis* isomer $M(CO)_4LL'$ only was the reaction product, some runs were carried out in other solvents where better band resolution allowed such characterization. Kinetic data for such solvents (*n*-heptane, carbon tetrachloride, etc.) are not reported here, though, owing to the very low solubility of the examined carbonyl derivatives. Unfortunately, attempts to prepare and isolate the "mixed" reaction products *cis*-$Mo(CO)_4LL'$ as pure substances failed since the reactions led to equilibrium mixtures. The infrared data were obtained with a Perkin-Elmer Model 621 spectrophotometer. The reactions were carried out under nitrogen in an aluminum-foil-wrapped vessel fitted with a serum cap. More details about this method have been given previously.[6] Reaction mixtures for which the product was not isolated gave infrared spectra analogous to the disubstituted derivatives *cis*-$Mo(CO)_4L_2$ (Table I).

Results and Discussion

In Table I there are listed the CO stretching frequencies of the molybdenum carbonyls investigated along with those of authentic samples of products independently prepared when possible. By allowing $Mo(CO)_5L$ to react with neutral ligands L', *cis*-$Mo(CO)_4$-LL' complexes only have been obtained. These could

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TABLE I
CO Stretching Frequencies (cm^{-1}) of Some
Molybdenum Carbonyl Derivatives[a]

Compounds	ν_{CO}				Solvent
Mo(CO)$_5$(4-pic)	2072 w	1980 w	1935 vs	1902 sh	CHCl$_3$
Mo(CO)$_5$(py)	2072 w	1978 w	1935 vs	1904 sh	CHCl$_3$
cis-Mo(CO)$_4$(4-pic)$_2$	2019 m	1901 m	1882 sh	1835 s	CH$_3$CN
cis-Mo(CO)$_4$(py)$_2$	2024 m	1905 m	1881 sh	1837 s	CH$_3$CN
cis-Mo(CO)$_4$(4-pic)(3,4-lut)	2019 m	1893 vs	1874 sh	1828 s	CH$_3$CN
cis-Mo(CO)$_4$(4-pic)(3-Cl(py))	2024 m	1906 vs	1886 sh	1836 s	CH$_3$CN

[a] All spectra recorded on a Perkin-Elmer Model 621 spectrophotometer. Abbreviations: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder.

not be isolated but were characterized by their infrared spectra in the reaction mixture. The general reaction investigated is

$$Mo(CO)_5L + L' \longrightarrow cis\text{-}Mo(CO)_4LL' + CO \quad (1)$$
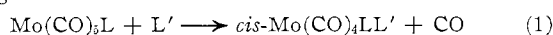
where L and L' are ligands having nitrogen, phosphorus, arsenic, and antimony as donor atoms, in toluene.

In Table II we report the pseudo-first-order rate constants, k_{obsd} (sec^{-1}), for reaction 1. The values of the pseudo-first order rate constants fit the two-term rate law

$$k_{obsd} = k_1 + k_2[L'] \quad (2)$$

The values of k_1 and k_2 are reported in Table III.

TABLE II
Pseudo-First-Order Rate Constants, k_{obsd}, for the Reaction
Mo(CO)$_5$L + L' $\longrightarrow$ cis-Mo(CO)$_4$LL' + CO,
in Toluene at 70°

Rates for Mo(CO)$_5$(4-pic)

L' = 3,4-Lutidine		L' = 3-Chloropyridine		L' = 4-Picoline	
[L'], M	10$^5k_{obsd}$, sec^{-1}	[L'], M	10$^5k_{obsd}$, sec^{-1}	[L'], M	10$^5k_{obsd}$, sec^{-1}
0.230	12.5	0.159	8.06	0.112	9.98
0.544	19.6	0.298	8.42	0.210	12.6
0.664	22.4	0.516	9.67	0.432	16.6
0.820	25.3	0.895	11.0	0.705	22.2
1.05	32.8	1.30	12.8	0.908	24.8
1.31	37.2			1.17	29.7

Rates for Mo(CO)$_5$(py) + py

[L'], M	10$^5k_{obsd}$, sec^{-1}
0.148	8.05
0.418	11.1
0.514	11.8
0.899	15.4
1.08	17.3
1.39	20.7

TABLE III
Rate Constants for the Reaction
Mo(CO)$_5$L + L' $\longrightarrow$ cis-Mo(CO)$_4$LL' + CO,
in Toluene at 70°

Mo(CO)$_5$L	L'	10$^5k_1$, sec^{-1}	10$^4k_2$, M^{-1} sec^{-1}
Mo(CO)$_5$(4-pic)	3,4-Lutidine	8	2.4
Mo(CO)$_5$(4-pic)	4-Picoline	8	1.7
Mo(CO)$_5$(4-pic)	3-Chloropyridine	8	0.43
Mo(CO)$_5$(py)	Pyridine	6	1.1
Mo(CO)$_6$[a]	P(C$_6$H$_5$)$_3$	~20	1.77

[a] Data at 112° from ref 13.

According to the long-accepted interpretation of analogous kinetic results,[4,7-10] the k_1 term of eq 2 is ascribed to a simple slow dissociation of a CO group from Mo(CO)$_5$L

$$Mo(CO)_5L \xrightarrow[\text{slow}]{-CO} [Mo(CO)_4L] \xrightarrow[\text{fast}]{+L'} cis\text{-}Mo(CO)_4LL' \quad (3)$$
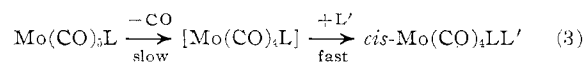
As for the k_2 term, the possibility that it represents a bimolecular attack of the entering aromatic amine on the CO group of the substrate followed by rearrangement appears rather unrealistic, although such attack may be likely for other reactions, like those of Ir(CO)$_3$L$_2$$^+$ and M(CO)$_6$$^+$ (M = Mn, Re) with alkoxide ions.[11,12] We are inclined to believe that the k_2 term corresponds to a direct displacement of CO by L' in a seven-coordinated activated complex

$$Mo(CO)_5L + L' \longrightarrow [Mo(CO)_5LL'] \longrightarrow Mo(CO)_4LL' + CO \quad (4)$$
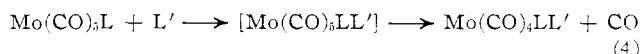
Similar interpretation has been given for the attacking ligand-dependent term of the rate law describing some substitution reactions of Mo(CO)$_4$(dipy) with phosphites[8] and of molybdenum hexacarbonyl with phosphines leading to monosubstituted products.[13]

Rate data (Table III) for the dissociative path relative to the compounds Mo(CO)$_5$(amine) indicate that a *cis* effect, if any, is very small, notwithstanding the different σ-donor ability of 4-picoline compared to pyridine so far as this is reflected by the proton basicities. It is to be noted that these two ligands may prove indistinguishable from a steric point of view. A recent study[14] of infrared spectra of W(CO)$_5$L (L = aliphatic or aromatic amines, pyridine, phosphine) has shown that the CO stretching shift on changing the ligand L is affected only by the σ-donor ability of L. However, the extent to which the CO stretching frequencies are reliable indexes of the M-C bond strength in octahedral carbonyl derivatives is still open to question.[15] Substitution rates for complexes with ligands having P, As, or Sb donor atoms were too slow to measure. The bulkiness of the L groups increases on going from N-donor to the last three donor ligands. Steric reasons should instead suggest a steric acceleration for such a change of ligands. Thus, in the case of manganese and rhenium carbonyl derivatives, M(CO)$_4$-XL, the dissociative term k_1 increases as the steric requirements of ligand L increase.

Seemingly, the observed kinetic *cis* effect for Mo(CO)$_5$L reactions must originate from factors other than those related to spatial requirements, such as electronic properties of L ligands. The pyridine derivative is almost as reactive as the substituted pyridine

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complex, but it reacts much faster than the molybdenum hexacarbonyl or the MR_3 carbonyl derivatives. To the extent that such effect, as observed, is attributable to a stronger Mo–C bond in the starting complex, one can surmise that it results from a rather delicate balance of σ-donating and π-accepting abilities of the coordinated ligands not yet fully understood. The relative importance of the steric and electronic properties of ligand L in determining the *cis* effect seems to depend on the metal atom also. Further testing of this observation was not feasible since rates of reactions analogous to that represented by eq 1 for chromium and tungsten carbonyl derivatives were too slow to be measured.

As for the k_2 term, the reactivity order for the reactions of $Mo(CO)_5$(4-pic) is 3,4-lutidine > 4-picoline > 3-chloropyridine, reflecting the decreasing proton basicity order of these amines. Such correlation between nucleophilic reactivity and proton basicity has long been recognized as a general feature of bimolecular substitution on carbonyl derivatives, among which tetracarbonyl halide dimers of rhenium and manganese, $[M(CO)_4X]_2$, might be mentioned.[6,16] The extremely low reactivity of $Mo(CO)_5MR_3$ is likely to be due to steric hindrance to bimolecular attack of the bulky reagent species.

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Some Properties of Several Trimethylplatinum(IV) Compounds

BY G. R. HOFF AND C. H. BRUBAKER, JR.

Trimethylplatinum(IV) iodide was first prepared in 1909 by Pope and Peachey,[1] and later Menzies and Overton[2] reported that a yellow form of the compound was tetrameric in benzene but that the white form, which they prepared by adding potassium iodide to a solution of trimethylplatinum(IV) sulfate, was dimeric. The crystal structure of trimethylplatinum(IV) chloride was determined by Rundle and Sturdivant,[3] and it was also tetrameric. Trimethylplatinum(IV) compounds such as the hydroxide, nitrate, and sulfate[1] have been reported.[4–6] In this laboratory[7]

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we have been interested in trimethylplatinum compounds in connection with unsuccessful attempts to prepare tetramethylplatinum(IV) by the reaction of methylsodium with trimethylplatinum(IV) iodide.[8] The present note deals with the question of possible differences between the yellow and white forms of the trimethylplatinum(IV) iodide and the conductances of trimethylplatinum(IV) salts in aqueous solutions.

Experimental Section

Yellow $(CH_3)_3PtI$ was prepared by the method of Clegg and Hall;[9] the nitrate, the sulfate, and the white form of $(CH_3)_3PtI$ were prepared by the methods of Pope and Peachey[1] and Ivanova and Gel'man.[5]

Infrared spectra were determined by use of KBr disks, mineral oil, Fluorolube, and 1,3-hexachlorobutadiene mulls. A Unicam SP-200 spectrophotometer was used for the 650–5000-cm^{-1} region and a Beckman IR-7 spectrophotometer for the 200–650-cm^{-1} region.

X-Ray powder diffraction patterns were obtained with samples in 0.3-mm glass capillary tubes, a copper X-ray tube with nickel filter, and a 114.59-mm camera.

Molecular weights of the two forms of the $(CH_3)_3PtI$ were determined in benzene by use of a Mechrolab vapor pressure osmometer and a nonaqueous probe designed to operate at 37°. It was calibrated with benzil as a standard.

Conductance measurements of $(CH_3)_3PtNO_3$ and $[(CH_3)_3Pt]_2$-SO_4 solutions in water were made by use of a Wayne–Kerr B221 Universal bridge and a modified Shedlovsky cell.[10] The $[(CH_3)_3$-$Pt]_2SO_4$ was weighed as the tetrahydrate and portions were added successively to the cell which contained a known volume of water. Since the nitrate was deliquescent, it could not be weighed and introduced into the cell, but a concentrated solution was prepared by quantitative metathesis between a solution of known concentration of the sulfate and barium nitrate. The conductance of concentrated stock solution, in which the platinum content had been determined, was measured and it was diluted successively to make the more dilute solutions.

Results and Discussion

The first objective of this study was to compare the yellow and white forms of trimethylplatinum(IV) iodide and no differences could be found. The infrared spectra proved to be identical and the absorptions found compared very well with those previously reported for the yellow form.[7,11] A few minor differences were observed in the X-ray diffraction powder patterns, but they consisted only of an absence of a few very weak lines from one or the other pattern. The patterns compared favorably with that previously reported for the yellow form[7] (Table I).

Menzies and Overton[2] had determined the molecular weight of the iodides in benzene and reported association factors of 3.2–3.4 for the yellow form and 2.4 for the white form and they noted the white was converted to the yellow upon standing in warm or boiling benzene. In this study we have determined the association factors and find 4.01 ± 0.12 for the yellow form and 4.07 ± 0.08 for the white form. The yellow form is recovered if the solution of the white form is refluxed with benzene and then concentrated until crystallization occurs.

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