parallels the decrease in the discrimination between the complexes containing different leaving groups suggests that in the processes with the more efficient thioethers bond formation in the transition state is the driving force of the reaction. A marked dependence of the rate upon the nature of the entering group is to be expected under these circumstances. A residual dependence of rate upon the nature of the leaving amine is not inconsistent with a situation with virtually no bond breaking in the transition state, since the σ-donor properties of the amine will influence the electrophilicity of the reaction center. It implies a fairly compact transition state, which might be related to the fact that in these reactions both the entering and leaving groups are neutral and therefore repel one another least of all.

It is of interest to compare the behavior of thioethers as nucleophiles toward these Au(III) species with that toward Pt(II) derivatives. It has been suggested[2] that also in the reactions of RSR′ toward Pt(II) substrates bond making is the driving force of the reaction. It seems that thioethers favor the formation of the new bond without promoting at the same time a significant breaking of the old one. There are however significant differences. Apart from the greater reactivity of the Au(III) species, which seems to be a general rule,[7] it is found that, whereas the discrimination between different leaving groups is independent of the nature of the entering thioether for the reactions at platinum(II) complexes, the limiting behavior is only achieved in the case of gold(III) complexes with the most reactive thioethers. This might be related to the greater ability of Pt(II) to support a nonsynchronous substitution mechanism.[7]

In addition, the nucleophilicity of RSR′ toward Pt(II) is related quite simply to the inductive effects of the radicals bonded to the sulfur atoms[2] (see Table II, note *b*), whereas the same is not true in the present case. This might be attributed to the steric hindrance effects, which are of greater importance in Au(III) than in Pt(II). The only reagent which, because of its structure, might be not significantly affected by steric hindrance is tetrahydrothiophene; this is the most reactive thioether that was used.

Experimental Section

The complexes of the type $AuCl_3(am)$ were prepared as described previously.[1] The complex $AuCl_3((C_2H_5)_2S)$ was obtained with the method described in the literature.[8] The thioethers were commercial samples, reagent grade. The solvent, acetone, was purified and dried by successive distillation over $KMnO_4$ and K_2CO_3.

Kinetics. The reactions were followed spectrophotometrically, as already described in the case of dibenzyl sulfide.[1] Known volumes of the complex and reagent in acetone were brought separately to the reaction temperature and mixed in the thermostated cell of an Optica CF4 double-beam recording spectrophotometer. The solutions of the complexes in acetone obey Beer's law and are stable. Once the spectrum changes characteristic of the reacting system were determined, the kinetics were followed by observing the wavelength at a chosen value (usually 340 mμ) and recording the change of optical density as a function of time.

Acknowledgments.—We thank Dr. M. L. Tobe for stimulating discussions and the Italian Council for Research (CNR, Rome) for financial support.

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[8] P. C. Ray and D. C. Sen, *J. Indian Chem. Soc.*, **7**, 67 (1930).

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Reactivity of Thioethers toward Neutral Palladium(II) Complexes

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The rates of displacement of one amine (am) from complexes of the type *trans*-$Pd(am)_2Cl_2$ by a variety of thioethers have been measured in 1,2-dimethoxyethane at 25°. The reactivity increases linearly with the increasing σ-donor ability of the entering nucleophile, RSR′, and decreases linearly with the basicity of the amine. Moreover, the discrimination of each substrate between the various thioethers is independent of the nature of the amine, and the discrimination of each reagent between various substrates is independent of the nature of the thioether. This is discussed in terms of an associative mechanism of reaction.

Introduction

In previous works[1,2] the nucleophilicity of thioethers toward platinum(II) and gold(III) planar complexes has been investigated. The kinetics of the reactions

$$Pt(bipy)(C)X + RSR' \longrightarrow Pt(bipy)(C)(RSR')^+ + X^-$$

($C, X = NO_2, Cl;\ NO_2, NO_2;\ NO_2, N_3;\ N_3, Cl;\ Cl, Cl$) and

$$AuCl_3(am) + RSR' \longrightarrow AuCl_3(RSR') + am$$

(am = pyridine derivatives) have been studied for a variety of thioethers, RSR′, and complexes. The results indicate that these substitutions occur through an associative mechanism where the transition state is mainly determined by the formation of the new bond between the metal and the entering group. It implies that the

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[1] L. Cattalini, M. Martelli, and G. Kirschner, *Inorg. Chem.*, **7**, 1488 (1968).

[2] L. Cattalini, M. Martelli, and G. Marangoni, *ibid.*, **7**, 1492 (1968).

intimate mechanism is not synchronous in the sense that the reaction proceeds through the formation of a labile five-coordinated intermediate which then dissociates to give the product. Therefore, the change of the nature of the leaving group is expected to influence the rate of substitution mainly because it causes a different electrophilicity at the reaction center and not through a different degree of bond breaking in the transition state.

The extension of the studies to palladium(II) derivatives can provide further information about this argument. In fact, the concept that the utilization of five orbitals for covalent bonding becomes progressively more difficult as the effective nuclear charge of the metal increases[3] implies a greater tendency for the formation of a relatively stable reaction intermediate on going from Au(III) to Pt(II)[4] and from Pt(II) to Pd(II).

In this paper we report the kinetic data relative to the processes

$$trans\text{-Pd(am)}_2\text{Cl}_2 + \text{RSR}' \longrightarrow trans\text{-Pd(am)(RSR}')\text{Cl}_2 + \text{am} \quad (1)$$

in 1,2-dimethoxyethane at 25°.

Results

Examination of the changing spectrum of the reaction mixture containing the appropriate complex and thioether shows that the initial absorbance corresponds exactly to that of the starting complex and changes with time in a first-order fashion. This first reaction is followed by a second one, much slower, and the final spectrum is that of the complex *trans*-$\text{Pd(RSR}')_2\text{Cl}_2$. The optical density at the end of the first step corresponds to that measured, under the same conditions, by mixing solutions of $\text{Pd}_2(\text{RSR}')_2\text{Cl}_4$ and amine at the appropriate concentration, *i.e.*, to the optical density of the complex *trans*-$\text{Pd(am)(RSR}')\text{Cl}_2$. Therefore, the kinetics of the first step, which are reported, refer to process 1.

The kinetics were followed spectrophotometrically, by carrying out the reactions in the presence of a large excess of the entering reagent in order to realize pseudo-first-order conditions. The rate constants, k_{obsd}, were obtained from the plot of log $(D_t - D_\infty)$ *vs.* time, where D_t and D_∞ are the optical densities of the reaction mixture at 340 mμ at time t and at the end of the first stage, respectively. Measurements carried out at other wavelengths where there is an adequate change of optical density give the same value for the rate constant. The values of k_{obsd} are summarized in Table I.

Discussion

The dependence of the observed rate constant upon the concentration of the entering reagent obeys the equation $k_{\text{obsd}} = k_2[\text{RSR}']$. There is no significant first-order contribution to the rate law. The second-

Table I

First-Order Rate Constants, k_{obsd}, Relative to Reaction 1 in 1,2-Dimethoxyethane at 25°[a]

[RSR'], M	10^2k_{obsd} sec^{-1}	[RSR'], M	10^2k_{obsd} sec^{-1}
(1) RSR' = Tetrahydrothiophene			
3-Cyanopyridine		Pyridine	
0.03	1.8	0.23	0.32
0.06	3.4	0.46	0.63
0.12	7.4	4-Methylpyridine	
4-Cyanopyridine		0.233	0.15
0.06	1.68	0.466	0.3
0.12	3.43	1.165	0.7
0.30	8.74		
(2) RSR' = Diethyl Sulfide			
3-Cyanopyridine		Pyridine	
0.028	1.35	0.13	0.155
0.056	2.6	0.26	0.33
0.112	5.15	0.43	0.65
0.224	10.9	4-Methylpyridine	
4-Cyanopyridine		0.3	0.185
0.082	2.4	0.5	0.31
0.11	3.1	0.75	0.46
0.164	4.6	Morpholine	
0.328	9.3	0.8	0.044
		1.12	0.062
		2.24	0.13
(3) RSR' = Ethyl Methyl Sulfide			
3-Cyanopyridine		Pyridine	
0.082	3.45	0.592	0.56
0.164	6.7	1.184	1.3
0.328	13.3	1.58	1.64
4-Cyanopyridine		4-Methylpyridine	
0.04	1.05	0.584	0.245
0.08	2.0	0.778	0.32
0.2	4.9	1.178	0.495
0.4	10		
(4) RSR' = Dibenzyl Sulfide			
3-Cyanopyridine		Pyridine	
0.083	1.35	0.227	0.085
0.166	2.65	0.333	0.14
0.332	5.2	0.667	0.27
4-Cyanopyridine		4-Methylpyridine	
0.091	0.83	0.151	0.027
0.227	2.05	0.303	0.055
0.455	4.2	0.667	0.12
(5) RSR' = Phenyl Methyl Sulfide			
3-Cyanopyridine		Pyridine	
0.083	0.74	0.42	0.1
0.166	1.45	1.05	0.27
0.332	3.0	2.1	0.51
4-Cyanopyridine		2.8	0.7
0.16	0.83	4-Methylpyridine	
0.321	1.76	0.434	0.05
0.535	2.80	1.085	0.121
1.6	8.5	2.17	0.254
(6) RSR' = Diisopropyl Sulfide			
3-Cyanopyridine			
0.1	0.35		
0.2	0.75		
1.0	3.66		

[a] The concentration of the substrate in the reaction mixture was always of the order of magnitude of 10^{-4} M.

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(3) R. S. Nyholm, *Proc. Chem. Soc.*, 273 (1961); R. S. Nyholm and M. L. Tobe, *Experientia Suppl.*, **9**, 112 (1965).

(4) L. Cattalini, A. Orio, and M. L. Tobe, *J. Am. Chem. Soc.*, **89**, 3130 (1967).

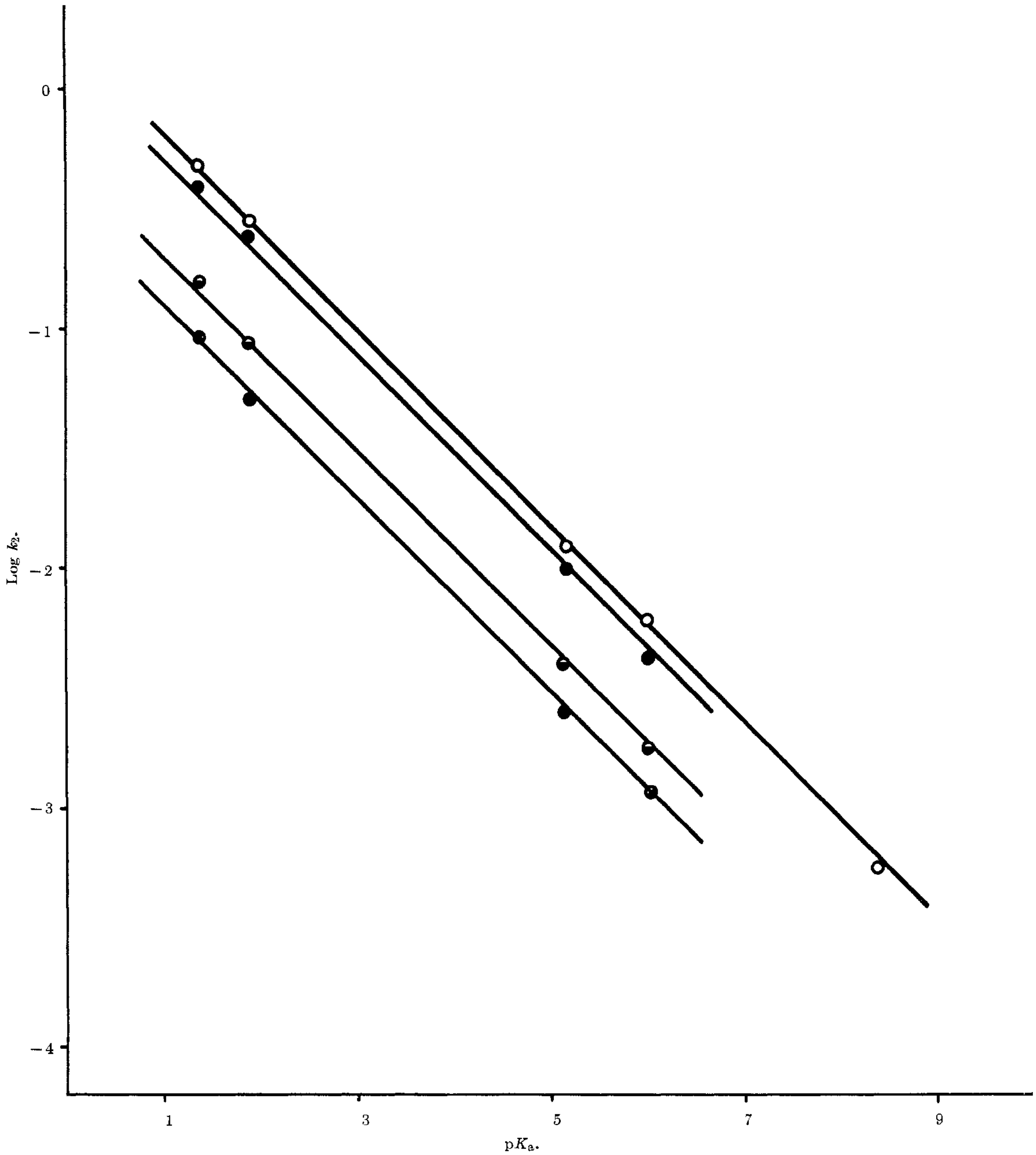

Figure 1.—Plot of log k_2 against the pK_a of the leaving amine: ○, RSR′ = diethyl sulfide; ●, RSR′ = methyl ethyl sulfide; ◐, RSR′ = dibenzyl sulfide; ⊗, RSR′ = phenyl methyl sulfide.

order rate constants, k_2, are summarized in Table II, together with the parameters (pK_a and $-\Sigma\sigma^*$) which give a relative measure of the σ-donor ability of the amines and thioethers, respectively. As expected, the reactivity increases with the σ-donor ability of the entering nucleophile and decreases with the σ-donor ability of the amine.

We must point out, first of all, that by changing the substrate in the series *trans*-Pd(am)$_2$Cl$_2$ we change the nature of the leaving group as well as that of the ligand *trans* to it. However, if the transition state corresponds to a structure where the bond between the metal and the leaving amine is not significantly broken, the influence of the two amine molecules upon its stability is expected to be the same. In fact, by assuming the usual[5] trigonal-bipyramidal structure for the transition state, both amine molecules will occupy equivalent positions in the trigonal plane, whereas the entering reagent will be in the third position and the two chloride ligands, originally *cis* to the amine in the ground state, will occupy the apical positions.

The associative mechanism, which has been proposed for substitution on planar substrates,[5] is in accord with the fact that the plot of log k_2 *vs.* the pK_a of the amine gives parallel straight lines for the thioethers studied (Figure 1). In fact, the discrimination of the reagents between different complexes is insensitive to the nature of the thioether and the discrimination of

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(5) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin Inc., New York, N. Y., 1965, Chapter II and references therein.

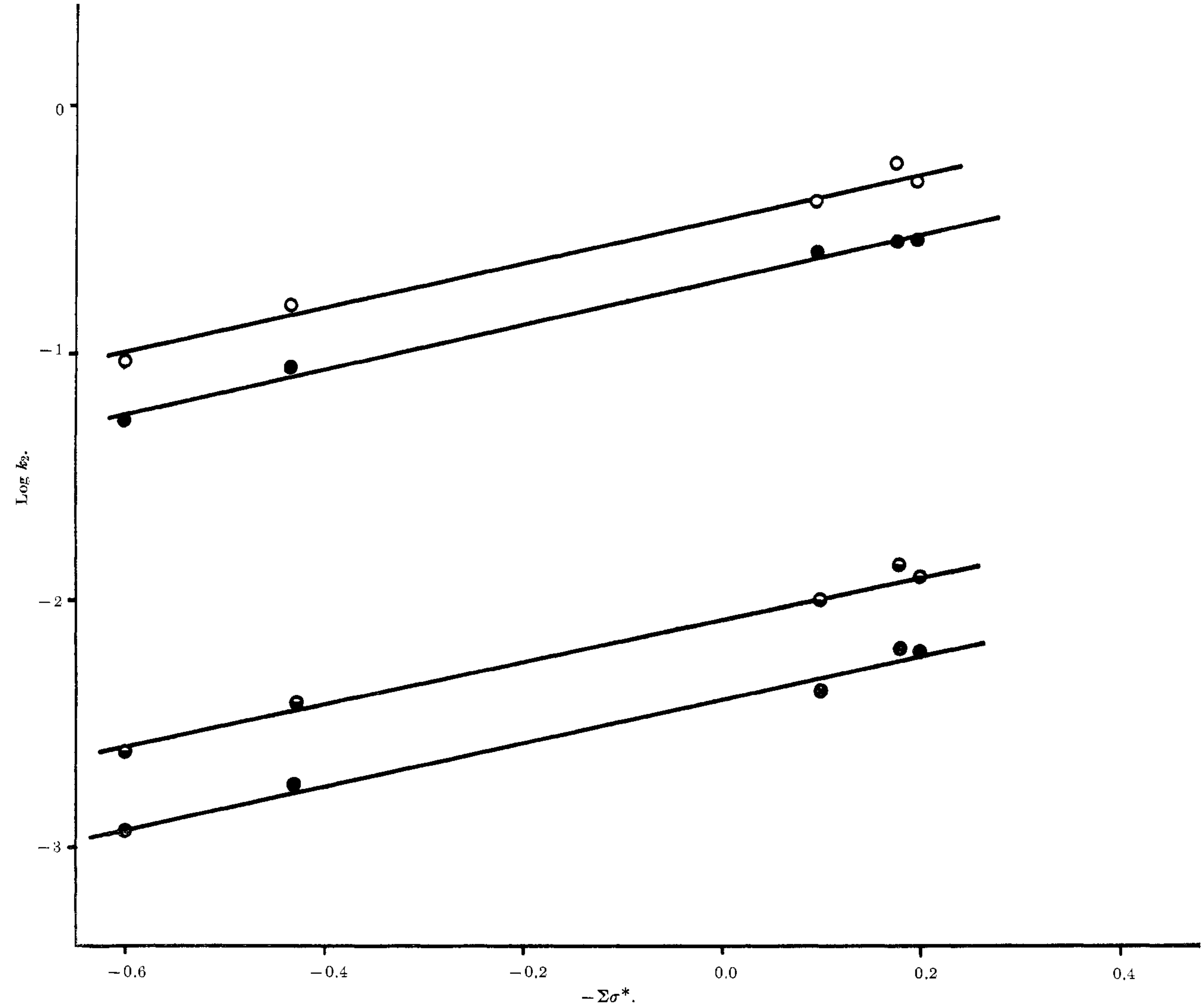

Figure 2.—Plot of log k_2 against the value of $-\Sigma\sigma^*$ of the entering thioether: ○, am = 3-cyanopyridine; ●, am = 4-cyanopyridine; ◒, am = pyridine; ⊗, am = 4-methylpyridine.

TABLE II

SECOND-ORDER RATE CONSTANTS, k_2, RELATIVE TO REACTION 1 IN 1,2-DIMETHOXYETHANE AT 25°

		10^3k_2, M^{-1} sec^{-1}					
Amine	pK_a[a]	tht[b] (0.18)[c]	$(C_2H_5)_2S$ (0.2)	CH_3S-C_2H_5 (0.1)	Bz_2S (−0.43)	C_6H_5S-CH_3 (−0.6)	$(i\text{-}C_3H_7)S$ (+0.38)
3-Cyanopyridine	1.38	590	470	410	160	89	36
4-Cyanopyridine	1.90	280	285	250	90	53	...
Pyridine	5.17	13.8	12.3	10	4.0	2.5	...
4-Methylpyridine	6.02	6.3	6.15	4.2	1.8	1.15	...
Morpholine	8.4	...	0.56	...	...	...	...

[a] Values relative to the acids amH$^+$ in water: D. D. Perrin, "Dissociation Constants of Organic Bases in Aqueous Solution," Butterworths and Co. Ltd., London, 1965; and L. G. Sillén and A. E. Martell, "Stability Constants," Special Publication No. 17, The Chemical Society, London, 1964. [b] tht = tetrahydrothiophene. [c] The values in parentheses are the sum of the Taft σ^* values ($-\Sigma\sigma^*$) relative to the radicals R and R′ bonded to sulfur in RSR.′

the complexes between the various entering groups is insensitive to the nature of the amine.

The slope of the lines in Figure 1 (−0.7) is higher than that measured for planar d^8 complexes containing only one amine.[2,6] One reason for this may be that the donor ability of *two* amine ligands (*i.e.*, the leaving group and the *trans* partner) influences, in the present case, the electrophilicity of the center of the reaction. Therefore, the high slope cannot be taken as evidence for high leaving-group effect.

A linear relationship is also observed, for each substrate, in the plot of log k_2 *vs.* the sum of the Taft σ^* values[7] relative to the inductive effects of the radicals bonded to sulfur in RSR′ (Figure 2). (The exception represented by diisopropyl sulfide is likely to be due to steric hindrance retardation effects.) The same behavior was observed in the reactions of thioether toward platinum(II) substrates.[1] A proper comparison cannot be made, because of the different nature of the leaving group and solvent, but one can observe that, in this case also, alkyl and aryl thioethers behave in the same way. It probably indicated the absence of a

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[6] L. Cattalini and M. L. Tobe, *Inorg. Chem.*, **5**, 1145 (1966); L. Cattalini, A. Orio, and M. L. Tobe, *ibid.*, **6**, 75 (1967).

[7] The values of σ^* reported in Table II are from R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newmann, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956. See also H. K. Hall, Jr., *J. Am. Chem. Soc.*, **79**, 5441 (1957), and references therein.

significant π-bonding contribution to the energetics of substitution.

Finally, the fact that the displacement of the second amine molecule is much slower than that of the first one indicates that in these complexes the *trans*-labilizing effect of the amine is higher than that of thioethers. Since other observations show that thioethers are easily replaced by amines from the complexes *trans*-$Pd(RSR')_2Cl_2$, we must conclude that a good *trans* labilizer is at the same time a good entering reagent. This seems to be a general rule for the reactions at platinum(II) substrates[5] and it agrees with the proposed associative mechanism *via* the trigonal-bipyramidal transition state, owing to the equivalence of the leaving group and the *trans* partner in the transition state. The increasing number of available data relative to the substitutions on Pd(II) complexes seems to confirm the expected similarity of behavior between Pt(II) and Pd(II) derivatives.

Experimental Section

The complexes *trans*-$Pd(am)_2Cl_2$ were obtained by following the methods reported in the literature.[8] The analytical figures correspond to the proposed formula, and the melting points, to the values reported in the literature.[8] Thioethers were pure commercial samples, and the solvent, 1,2-dimethoxyethane, was distilled over sodium before use.

Kinetics.—The method used to follow the kinetics was similar to that reported previously.[1,2] Known volumes of thermostated solutions of the complex and reagent were mixed in the thermostated cell of an Optica CF4 double-beam recording spectrophotometer. The spectral changes characteristic of the reacting system were first determined by scanning the near-ultraviolet region of the spectrum at known intervals. Afterward, a suitable wavelength was chosen to study the reaction (usually 340 mμ) and the kinetics were followed by recording the changes of optical density as a function of time.

Acknowledgments.—We thank the Italian Council for Research (CNR, Rome) for financial support.

(8) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., New York, N. Y., 1936.

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Lewis Adducts of the $Fe(CO)_4^{2-}$ and $Co(CO)_4^-$ Ions

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The metal carbonyl anions $Fe(CO)_4^{2-}$ and $Co(CO)_4^-$ form adducts with indium tribromide or gallium tribromide of the type $M(CO)_4M'Br_3^{n-}$. The complex ion $Fe(CO)_4InBr_3^{2-}$ dissociates in solution to give a new ion $Fe(CO)_4InBr_2^-$. This new ion will form adducts with amines and the preparation of the ions $Fe(CO)_4InBr_2 \cdot (C_2H_5)_3N^-$ and $Fe(CO)_4InBr_2 \cdot C_5H_5N^-$ is also described.

The ability of metal carbonyls to react with numerous Lewis bases has been well documented, whereas the ability of pure metal carbonyl anions to function as Lewis bases has received only slight attention. The first examples of such adducts to be reported were the complex anions $Mn(CO)_5BH_3^-$ and $(C_6H_5)_3PMn(CO)_4BH_3^-$.[1] More recently complex anions of the type $M(CO)_5Mn(CO)_5^-$ (where M = Cr, Mo, or W) were obtained by the direct interaction of the Lewis base $Mn(CO)_5^-$ and the group VI metal carbonyl.[2] In a similar manner, the adduct $W(CO)_5Co(CO)_4^-$ was prepared.[3] Indium tribromide also forms stable adducts with the $Cr(CO)_5^{2-}$ and $W(CO)_5^{2-}$ anions although the synthetic route to these materials does not involve the direct combination of the components.[4]

Experimental Section

All operations described herein, except the weighing of reactants and products, were carried out under a nitrogen atmosphere. The analytical data for the compounds prepared in this study are summarized in Table I.

Materials.—The metal carbonyl anions were prepared and isolated as described previously.[3] The anhydrous metal halides were obtained from Alfa Inorganics, Inc. and used without further purification.

Preparation of $[(C_6H_5)_3P]_2NCo(CO)_4MBr_3$ (M = In or Ga).—The preparation of both of the adducts was performed in an analogous manner. Therefore only the preparation of the indium derivative will be described. To a 1.41-g sample of $[(C_6H_5)_3P]_2NCo(CO)_4$ dissolved in 40 ml of CH_2Cl_2, a 0.72-g sample of $InBr_3$ was added. The mixture was stirred for 0.5 hr and filtered and then concentrated to 20 ml. A 1.45-g sample of product was obtained upon the addition of approximately 80 ml of ether.

Preparation of $[(C_6H_5)_3P]_2NCo(CO)_4CdBr_2 \cdot (C_2H_5)_2O$.—Cadmium dibromide, 0.28 g, was added to a solution of 0.74 g of $[(C_6H_5)_3P]_2NCo(CO)_4$ in 25 ml of tetrahydrofuran (THF). The mixture was stirred for 15 min, and then the solvent was removed under reduced pressure. The residue was dissolved in 20 ml of CH_2Cl_2 and filtered. The addition of 30 ml of ether resulted in the crystallization of 0.73 g of product. A proton nmr spectrum showed the presence of ethyl groups as well as phenyl groups but gave no evidence for the presence of THF. The area ratio of the phenyl groups to ethyl groups was 3.1:1.0.

Preparation of $[[(C_6H_5)_3P]_2N]_2Fe(CO)_4InBr_3$.—(A) A mixture of 0.51 g of $Fe_3(CO)_{12}$, 25 g of 1% sodium amalgam, and 40 ml of THF was stirred overnight. The excess amalgam was drained out of the bottom of the flask and then 0.7 g of $InBr_3$ was added to the mixture. After stirring 15 min, 2.5 g of $[(C_6H_5)_3P]_2NBr$ in 100 ml of CH_2Cl_2 was added to the mixture. It was then filtered and the filtrate was evaporated to dryness under reduced pressure.

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(1) G. W. Parshall, *J. Am. Chem. Soc.*, **86**, 361 (1964).

(2) A. Anders and W. A. G. Graham, *ibid.*, **89**, 539 (1967).

(3) J. K. Ruff, *Inorg. Chem.*, in press.

(4) J. K. Ruff, *ibid.*, **6**, 2080 (1967).