CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
IOWA STATE UNIVERSITY, AMES, IOWA 50010

Synthesis and Reactions of Isocyanatopentacarbonylrhenium(I)

BY ROBERT J. ANGELICI*[1] AND GARY C. FABER

Received August 5, 1970

The isocyanato complex $Re(CO)_5(NCO)$ has been prepared by treating $Re(CO)_6^+$ with either azide ion or hydrazine. With iodide ion, $Re(CO)_6^-$ yields $Re(CO)_5I$. Both $Re(CO)_6^+$ and $Re(CO)_5(NCO)$ react with primary amines (RNH_2) to give the previously known *cis*-$Re(CO)_4(NH_2R)(CONHR)$. The reaction of $Re(CO)_5(NCO)$ with bidentate ligands (L-L) such as diphos, *o*-phen, and dipy[6] gives the substituted complexes $Re(CO)_3$(L-L)(NCO). Kinetic studies of these substitution reactions indicate that CO dissociation from the complex is rate determining and that rate constants for the series of complexes $Re(CO)_5X$ decrease in the order NCO > Cl > Br > I.

Introduction

In recent years it has been demonstrated that isocyanato complexes of transition metals may be prepared from certain metal carbonyls by two methods. One involves the reaction with azide ion as first reported[2] for $W(CO)_6$

$$W(CO)_6 + N_3^- \longrightarrow W(CO)_5(NCO)^- + N_2 \qquad (1)$$

The other[3] uses hydrazine as the source of nitrogen, *e.g.*

$$C_5H_5Fe(CO)_3^+ + 2NH_2NH_2 \longrightarrow C_5H_5Fe(CO)_2(NCO) + NH_3 + N_2H_5^+ \qquad (2)$$

Where comparisons have been made,[3] the azide reaction has frequently given a slightly better yield. This is particularly true of uncharged metal carbonyl complexes such as $Cr(CO)_6$, $Mo(CO)_6$, or $W(CO)_6$. With cationic carbonyls, *e.g.*, $C_5H_5Fe(CO)_3^+$,[3] $C_5H_5Ru(CO)_3^+$,[4] or $Re(CO)_5(NH_2CH_3)^+$,[5] both routes are useful.

In the present paper, we describe the synthesis of $Re(CO)_5(NCO)$ from $Re(CO)_6^+$ by both the azide and hydrazine routes. The reaction of $Re(CO)_5(NCO)$ with diphos, *o*-phen, and dipy[6] to give $Re(CO)_3$(L-L)(NCO) has been studied kinetically. With isopropylamine, both $Re(CO)_5(NCO)$ and $Re(CO)_6^+$ yield *cis*-$Re(CO)_4(NH_2R)(CONHR)$.[5] The reactions of $Re(CO)_6^+$ with I^-, CN^-, and NCS^- have also been examined.

Experimental Section

General Data.—All reagents were obtained from commercial sources and used without further purification with the exception of materials employed in the kinetic studies. Infrared spectra were recorded on a Beckman IR-12 infrared spectrophotometer and were calibrated against known bands of polystyrene. Chemical analyses were performed by Schwarzkopf Microanalytical Laboratory and the mass spectra were recorded on an Atlas CH4 mass spectrometer at 70-eV electron energies.

The cation $Re(CO)_6^+$ was prepared according to a literature procedure[7] and precipitated as $[Re(CO)_6]B(C_6H_5)_4$ with $NaB(C_6H_5)_4$. In most instances the product was found to be pure enough for most synthetic purposes. It decomposed after long periods of exposure to air and could be purified by recrystallization from CH_2Cl_2–hexane.

Syntheses of new complexes were carried out in the minimum amount of solvent required to dissolve the $[Re(CO)_6]B(C_6H_5)_4$ and $Re(CO)_5(NCO)$ complexes.

Preparation of $Re(CO)_5(NCO)$.—To a solution of 0.33 g of $[Re(CO)_6]B(C_6H_5)_4$ (0.5 mmol) in acetone was added 0.03 g of NaN_3 (0.5 mmol) and the mixture was stirred under nitrogen for 6 hr or until no starting material was present as indicated by the infrared spectrum. During the reaction period gas evolution (N_2) was observed; when the reaction was complete, the solvent was removed *via* high vacuum, and the residue was extracted with 30 ml of $CHCl_3$. The white product was obtained by removal of the solvent *in vacuo*, recrystallization from $CHCl_3$–hexane, and drying under high vacuum; yield 0.10 g (55%). *Anal.* Calcd for $Re(CO)_5(NCO)$: C, 19.56; H, 0.00; N, 3.80. Found: C, 19.59; H, 0.00; N, 3.83. Infrared spectrum (CCl_4 solvent):[8] 2159 (w), 2048 (vs), 2020 (vw), 1995 (s) (C–O stretches); 2257 (m) (asymmetric NCO stretch).

Its mass spectrum shows the following ion fragments (and their relative intensities) with *m/e* values greater than 200: $Re(CO)_5(NCO)^+$, 90; $Re(CO)_4(NCO)^+$, 72; $Re(CO)_3(NCO)^+$, 66; $Re(CO)_4^+$, 69; $Re(CO)_2(NCO)^+$, 100; $Re(CO)_3^+$, 49; $Re(CO)(NCO)^+$, 72; $Re(CO)_2^+$, 43; $Re(CO)(CN)^+$, 53; $Re(NCO)^+$, 47; $ReCN^+$, 50; ReN^+, 66. For the fragments in which CO was lost, it was not determined whether the loss occurred from the NCO group or as a terminal CO group.

$Re(CO)_5(NCO)$ was also prepared using hydrazine. A CH_2Cl_2 solution of 0.20 g of $[Re(CO)_6]B(C_6H_5)_4$ and 0.15 ml of anhydrous hydrazine was stirred under a nitrogen atmosphere for 30 min. A white precipitate which had formed was removed by filtration. The presence of $Re(CO)_5(NCO)$ in the solution was established by comparing its infrared spectrum with that of $Re(CO)_5(NCO)$ as prepared above.

Preparation of $Re(CO)_3$(diphos)(NCO).—$Re(CO)_5NCO$ (72 mg) and diphos[6] (80 mg) were refluxed in $CHCl_3$ for 8 hr under nitrogen. The solvent was removed *in vacuo* and the white product was recrystallized from CH_2Cl_2–hexane. After drying under high vacuum a yield of 32 mg (55%) was obtained. *Anal.* Calcd for $Re(CO)_3$(diphos)(NCO): C, 52.84; H, 3.85; N, 2.06. Found: C, 53.27; H, 4.13; N, 2.58. Infrared spectrum ($CHCl_3$ solvent):[8] 2035 (s), 1958 (s), 1916 (s), (C–O stretches); 2250 (m) (asymmetric NCO stretch).

The ion fragments and their relative intensities in the mass spectrum are given for fragments with *m/e* greater than 598: $Re(CO)_3$(diphos)$(NCO)^+$, 23; $Re(CO)_2$(diphos)$(NCO)^+$, 30; Re(CO)(diphos)$(NCO)^+$, 78; Re(diphos)$(NCO)^+$, 100; Re(diphos)$(N)^+$, 33. In addition, the mass spectrum indicated other fragments of high mass whose pattern suggested the presence of polynuclear species. Polynuclear ions may result from decomposition of the sample since high temperatures were required to achieve sufficient volatility of the sample.

---

(1) Fellow of the Alfred P. Sloan Foundation, 1970–1972.

(2) W. Beck and H. S. Smedal, *Angew. Chem.*, **78**, 267 (1966); W. Beck, H. Werner, H. Engelmann, and H. S. Smedal, *Chem. Ber.*, **101**, 2143 (1968); H. Werner, W. Beck, and H. Engelmann, *Inorg. Chim. Acta*, **3**, 331 (1969).

(3) R. J. Angelici and L. Busetto, *J. Amer. Chem. Soc.*, **91**, 3197 (1969).

(4) A. E. Kruse and R. J. Angelici, *J. Organometal. Chem.*, **24**, 231 (1970).

(5) R. J. Angelici and A. E. Kruse, *ibid.*, **22**, 461 (1970).

(6) Abbreviations: diphos, 1,2-bis(diphenylphosphino)ethane; *o*-phen, 1,10-phenanthroline; dipy, 2,2′-dipyridyl.

(7) R. S. Nyholm, M. R. Snow, and M. H. B. Stiddard, *J. Chem. Soc.*, 6656 (1965).

(8) Frequencies given in cm^{-1}: s, strong; w, weak; m, medium; v, very; br, broad; sh, shoulder.

Preparation of $Re(CO)_3$(*o*-phen)(NCO).—A $CHCl_3$ solution of $Re(CO)_5(NCO)$ (50 mg) and *o*-phen[8] (25 mg) was refluxed under nitrogen for 5 hr. After removing the solvent *in vacuo*, the crude yellow product was recrystallized twice from CH_2Cl_2–hexane and then dried under high vacuum (yield 33 mg, 49%). *Anal.* Calcd for $Re(CO)_3$(*o*-phen)(NCO): C, 39.02; H, 2.08; N, 8.55. Found: C, 39.34; H, 2.14; N, 8.53. Infrared spectrum ($CHCl_3$):[8] 2026 (s), 1929 (s), 1908 (s) (C–O stretches); 2247 (m) (asymmetric NCO stretch).

Ion fragments and their relative intensities found in the mass spectrum are given for m/e values greater than 366: $Re(CO)_3$(*o*-phen)(NCO)$^+$, 48; $Re(CO)_2$(*o*-phen)(NCO)$^+$, 42; Re(CO)(*o*-phen)(NCO)$^+$, 31; Re(*o*-phen)(NCO)$^+$, 100; Re(*o*-phen)(N)$^+$, 93; Re(*o*-phen)$^+$, 34.

Reaction of $Re(CO)_5(NCO)$ with $(CH_3)_2CHNH_2$.—$Re(CO)_5(NCO)$ (36 mg) was stirred for 6 hr with isopropylamine (0.1 ml) in diethyl ether. During the reaction period a white precipitate formed. The solvent was removed *in vacuo*, and the residue was extracted with 25 ml of CH_2Cl_2. The product was identified as *cis*-$Re(CO)_4(NH_2R)(CONHR)$ (R = isopropyl) by comparing the infrared spectrum of the CH_2Cl_2 solution with that of the known compound[5] in the C–O stretching region.

Reaction of $Re(CO)_6^+$ with I^-, CN^-, and NCS^-.—An acetone solution of 50 mg of $[Re(CO)_6]B(C_6H_5)_4$ and 50 mg of $(C_4H_9)_4N^+I^-$ was refluxed under nitrogen for 30 min. The acetone was removed *in vacuo*, and the residue was extracted with CCl_4. The infrared spectrum in the C–O stretching region of this solution established[9] the presence of $Re(CO)_5I$.

A solution of 100 mg of $[Re(CO)_6]B(C_6H_5)_4$ in 20 ml of acetone was stirred with 300 mg of NaCN for 30 min. After removal of the solvent, the residue was extracted with 30 ml of CH_2Cl_2. Addition of hexane to this solution yielded a white precipitate which was dissolved in a minimum amount of water. The addition of a solution of $[(C_6H_5)_4As]Cl$ gave a white precipitate of $[(C_6H_5)_4As]Re(CO)_4(CN)_2$. The $Re(CO)_4(CN)_2^-$ complex has been reported previously.[10] The C–O stretching spectrum of the product (2090 (w), 2014 (s), 1990 (m), and 1916 (s, br)) is very similar to that[11] of *cis*-$Mn(CO)_4(CN)_2^-$ (2103 (w), 2029 (s), 2005 (m), 1936 (s, br)). Attempts to prepare $Re(CO)_5CN$ using lower concentrations of NaCN were unsuccessful. The attempted preparation of $Re(CO)_5(NCS)$ from $[Re(CO)_6]B(C_6H_5)_4$ and KNCS was also unsuccessful.

Reaction of $Re(CO)_6^+$ with $(CH_3)_2CHNH_2$.—To a solution of 190 mg of $[Re(CO)_6]B(C_6H_5)_4$ in acetone was added 1 ml of isopropylamine. An infrared spectrum[5] of the solution indicated that *cis*-$Re(CO)_4(NH_2R)(CONHR)$ (where R = isopropyl) was the product. This was further confirmed by treating the solution with trichloroacetic acid to give $Re(CO)_5(NH_2R)^+$. It is known[5] that *cis*-$Re(CO)_4(NH_2R)(CONHR)$ on treatment with acid yields $Re(CO)_5(NH_2R)^+$.

Kinetics. Preparation and Purification of Materials.—$Re(CO)_5NCO$ was prepared and purified as described. The ligands diphos (Strem Chemical Co.) and 2,2′-dipyridyl (Fisher) were used as obtained. 1,10-Phenanthroline monohydrate (Mallinckrodt) was refluxed in 2,2-dimethoxypropane for 1 hr; upon cooling, the *o*-phen crystallized and was collected. The compound was dried under high vacuum as the melt (120°) for several hours. The melting point of the resulting compounds was found to agree with that of the anhydrous material (117°). The solvent, toluene, was refluxed over sodium and carefully distilled. Preparations of the products $Re(CO)_3$(diphos)(NCO) and $Re(CO)_3$(*o*-phen)(NCO) have been described. The product $Re(CO)_3$(dipy)(NCO) was identified by comparing its infrared spectrum with that of the other products. In $CHCl_3$ solution, C–O stretching absorptions[8] occurred at 2026 (s), 1929 (s), and 1907 (s); the asymmetric NCO stretching absorption was observed at 2246 (m).

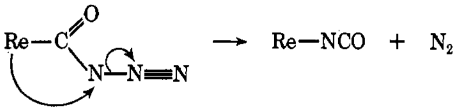
Determination of Rates.—Rates were determined by monitoring the disappearance of the low-energy carbonyl stretching frequency of $Re(CO)_5(NCO)$ at 1995 cm^{-1} with a Beckman IR-8 infrared spectrophotometer in a manner which has been described.[12] Activation parameters have been evaluated and error limits are one standard deviation.

Results and Discussion

Syntheses.—The cation $Re(CO)_6^+$ reacts with azide ion according to the equation

$$Re(CO)_6^+ + N_3^- \longrightarrow Re(CO)_5(NCO) + N_2 \qquad (3)$$

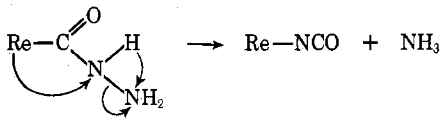
As with the isoelectronic $W(CO)_6$ (eq 1), the reaction probably proceeds by attack of N_3^- on a carbonyl carbon atom to produce an azide intermediate which rearranges with loss of N_2 to yield the isocyanate product



The isocyanate complex can also be prepared from $Re(CO)_6^+$ using hydrazine

$$Re(CO)_6^+ + 2NH_2NH_2 \longrightarrow Re(CO)_5(NCO) + NH_3 + N_2H_5^+ \qquad (4)$$

This reaction probably also occurs by initial attack of hydrazine on the carbonyl carbon atom. The resulting carbazoyl intermediate then rearranges with loss of NH_3 to yield $Re(CO)_5(NCO)$ again



Such a mechanism was postulated earlier for reaction 2.

With iodide ion, $Re(CO)_6^+$ reacts to give $Re(CO)_5I$

$$Re(CO)_6^+ + I^- \longrightarrow Re(CO)_5I + CO \qquad (5)$$

In an attempt to prepare $Re(CO)_5(CN)$ by an analogous reaction with excess cyanide ion, only $Re(CO)_4(CN)_2^-$ was obtained. With an excess of $Re(CO)_6^+$,

$$Re(CO)_6^+ + 2CN^- \longrightarrow Re(CO)_4(CN)_2^- + 2CO \qquad (6)$$

the reaction with CN^- yielded different products which have not yet been characterized. Likewise, products of the reaction with NCS^- have not yet been characterized.

With excess isopropylamine, $Re(CO)_6^+$ reacts rapidly to give the known[5] *cis*-$Re(CO)_4(NH_2R)(CONHR)$. The other products of this reaction have not yet been identified. The reaction of $Re(CO)_6^+$ with ammonia has been reported[13] to give $Re(CO)_5H$, urea, and NH_4^+. With tetramethylethylenediamine, $Re_2(CO)_{10}$ is produced.[14] Hence the reaction of amines with $Re(CO)_6^+$ is quite complicated and requires further study.

The $Re(CO)_5(NCO)$ reacts with isopropylamine (RNH_2) in the same way as does $Re(CO)_5Br$[5] to give *cis*-$Re(CO)_4(NH_2R)(CONHR)$

$$Re(CO)_5(NCO) + RNH_2 \longrightarrow cis\text{-}Re(CO)_4(NH_2R)(CONHR) + RNH_3^+NCO^- \qquad (7)$$

---

[9] J. C. Hileman, D. K. Huggins, and H. D. Kaesz, *Inorg. Chem.*, **1**, 933 (1962).

[10] W. Hieber and L. Schuster, *Z. Anorg. Allg. Chem.*, **287**, 214 (1956).

[11] R. J. Angelici, *Inorg. Chem.*, **3**, 1099 (1964).

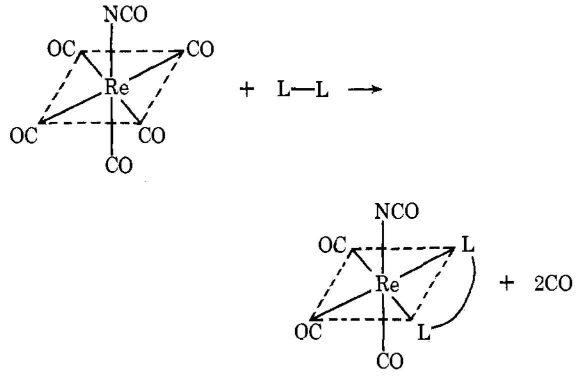
[12] G. C. Faber and R. J. Angelici, *ibid.*, **9**, 1586 (1970).

[13] H. Behrens and P. Pässler, *Z. Anorg. Allg. Chem.*, **365**, 128 (1969).

[14] E. W. Abel and S. P. Tyfield, *Can. J. Chem.*, **47**, 4627 (1969).

This reaction presumably proceeds by initial displacement of NCO^- to give $Re(CO)_5(NH_2R)^+$ which then reacts with additional amine to give the carboxamido product.

With bidentate ligands (L-L), $Re(CO)_5(NCO)$ reacts to give substitution products according to the equation



(8)

where L-L = diphos, *o*-phen, or dipy.[6] The presence of three strong C–O stretching absorptions in their infrared spectra supports[14,15] the geometry of the product shown in eq 8.

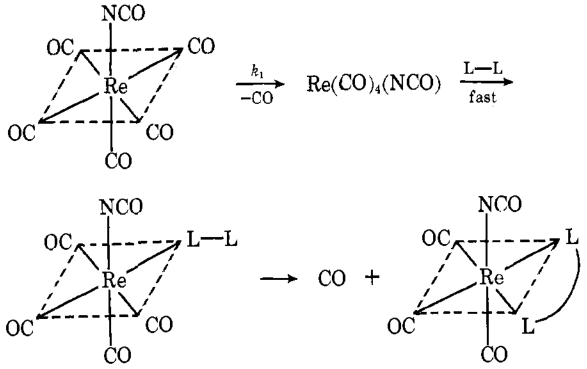
Kinetics of Reaction 8.—Pseudo-first-order rate constants for reaction 8 are given in Table I. The values of k_{obsd} do not depend upon the nature or concentration of the bidentate ligand and the reaction obeys a first-order rate law: rate = $k_1[Re(CO)_5(NCO)]$. This same rate law was obtained previously for the substitution reactions of $Re(CO)_5X$ (X = Cl, Br, I).[16] As in the $Re(CO)_5X$ reactions, we propose a mechanism in which rate-determining dissociation of one CO group is followed by rapid entry of one donor atom of the bidentate ligand (eq 9).

TABLE I

KINETIC DATA FOR THE REACTION[a] OF $Re(CO)_5NCO$ WITH BIDENTATE LIGANDS IN TOLUENE SOLVENT

Ligand	Concn, *M*	Temp, °C	10^4k_{obsd}, sec^{-1}
o-phen	0.053	45.0	1.83
o-phen	0.026		1.84
dipy	0.099		1.86
o-phen	0.015	55.1	6.24
o-phen	0.629		7.70
dipy	0.096		6.41
dipy	0.048		6.41
diphos	0.042		5.92
diphos	0.178		5.77
o-phen	0.311	60.0	13.58
dipy	0.065		10.00
dipy	0.032		9.78
diphos	0.029		8.75

[a] $\Delta H^{\ddagger} = 23.5 \pm 1.7$ kcal/mol. $\Delta S^{\ddagger} = 1.8 \pm 4.4$ eu.



(9)

For *o*-phen and dipy, there is no evidence in the infrared spectra of the reaction solutions for a complex $Re(CO)_4(L\text{-}L)(NCO)$, where the ligand is coordinated monodentately. In these cases the replacement of the second CO group must occur very rapidly. In contrast, there is infrared evidence for such an intermediate for the reaction with diphos. The same observations were made in the reactions of $Re(CO)_5X$. Rapid replacement of a second CO for the nitrogen donor ligands is similar to the fast reaction of $Re(CO)_4pyBr$ with additional pyridine to form $Re(CO)_3(py)_2Br$.[17] The slower replacement of this CO by the diphos ligand parallels the slow reaction of $Re(CO)_4[P(C_6H_5)_3]Br$ with $P(C_6H_5)_3$ to give $Re(CO)_3[P(C_6H_5)_3]_2Br$. As has been pointed out,[18] the presence of a nitrogen donor ligand in a metal carbonyl complex generally labilizes one or more of the remaining CO groups whereas in complexes which contain phosphorus donor ligands, the remaining CO groups are much less labile.

Table II summarizes the first-order rate constants and the activation parameters for the dissociation of CO from the $Re(CO)_5X$ complexes. The values of k_1 at 60° decrease with X in the order NCO > Cl > Br > I. The small effect of solvent on the rates of the $Re(CO)_5X$ reactions[16] allows this comparison of rates in different solvents to be made. The high rate of CO dissociation in $Re(CO)_5(NCO)$ indicates that the isocyanate ligand labilizes at least one CO group in the complex. It has been noted previously[18] that ligands with relatively "hard" donor atoms[19] have a notable tendency to labilize CO groups in $M(CO)_5X$ and $M(CO)_4X_2$ complexes. That N-bonded NCO is labilizing is consistent with the relatively "hard" (class a) character of the nitrogen donor atom.

TABLE II

KINETIC DATA FOR THE REACTIONS

$Re(CO)_5X + L\text{-}L \rightarrow Re(CO)_3(L\text{-}L)X + 2CO$

Compd	10^4k_1, sec^{-1} (at 60°)	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
$Re(CO)_5(NCO)^a$	10.5	23.5 ± 1.7	1.8 ± 4.4
$Re(CO)_5Cl^b$	4.2	30.5 ± 0.1	17.5 ± 0.3
$Re(CO)_5Br^b$	0.72	29.4 ± 1.8	10.7 ± 5.4
$Re(CO)_5I^b$	0.092	27.9 ± 5.6	2.2 ± 16.8

[a] In toluene solvent. [b] In CCl_4 solvent. From ref 16.

Attempts also have been made to correlate rates of CO dissociation in metal carbonyl complexes with their C–O stretching frequencies. In the present case, these absorptions occur at slightly higher absorptions

---

(15) R. J. Angelici, F. Basolo, and A. H. Poë, *J. Amer. Chem. Soc.*, **86**, 2215 (1963).

(16) F. Zingales, M. Graziani, F. Faraone, and U. Belluco, *Inorg. Chim. Acta*, **1**, 172 (1967).

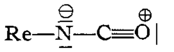
(17) F. Zingales, U. Sartorelli, and A. Trovati, *Inorg. Chem.*, **6**, 1246 (1967).

(18) R. J. Angelici, *Organometal. Chem. Rev.*, **3**, 173 (1968).

(19) R. G. Pearson, *J. Chem. Educ.*, **45**, 643, 581 (1968).

for the isocyanate complex than for the analogous chloride (CCl_4 solvent): for $Re(CO)_5(NCO)$, 2159 (w), 2048 (vs), 2020 (vw), 1995 (s); for $Re(CO)_5Cl$,[9] 2156 (w), 2045 (vw), 2016 (vw), 1982 (s). This suggests that there is greater Re–CO π bonding in the Cl complex than in the NCO derivative. From this one may infer that the Re–CO bond is weaker for the NCO complex and that CO dissociation should occur more rapidly, as is indeed the case. While the C–O stretching data and π-bonding arguments are consistent with the kinetic results in this case, this is frequently not true.[18] A more reliable approach to predicting rates of CO dissociation is to consider the "hard" and "soft" properties of the ligands in the complex.[18]

The relatively fast dissociation of CO from $Re(CO)_5(NCO)$ is caused by the low enthalpy of activation. This may occur because of weaker Re–CO bonds as suggested by the infrared data or because of a stabilization of the transition state by a resonance form of the ligand



$$\mathrm{Re{-}\overset{\ominus}{\underline{N}}{-}C{\equiv}\overset{\oplus}{O}|}$$

which places a high electron density on the N atom. This negative charge may then be donated to the Re to replace the electron density which is removed by the departing CO group. The entropy of activation (+1.8 eu) is somewhat low yet is in the range commonly found[18] for CO dissociation in other metal carbonyl derivatives.

Acknowledgment.—We are grateful to the National Science Foundation (GP-12136) for support of this research.

CONTRIBUTION FROM NOYES CHEMICAL LABORATORY,
UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS 61801

Reactions of $Cl_3MCo(CO)_4$ Compounds with Lewis Bases[1]

BY KAZUKO OGINO[2] AND THEODORE L. BROWN*

Received June 19, 1970

The reactions of $Cl_3MCo(CO)_4$ (M = Si, Ge, Sn) compounds with $P(OC_2H_5)_3$, $P(n\text{-}C_4H_9)_3$, and $P(C_6H_5)_3$ have been studied. Reaction of $Cl_3SnCo(CO)_4$ with $P(OC_2H_5)_3$, $P(n\text{-}C_4H_9)_3$, or $N(C_2H_5)_3$ in hexane or with THF in the neat solvent leads to formation of $SnCl_2[Co(CO)_4]_2$. The reaction appears to proceed *via* attack of the base at Sn, displacement of $Co(CO)_4^-$, and subsequent displacement of chloride from $Cl_3SnCo(CO)_4$ by $Co(CO)_4^-$. In the presence of excess base, products of the form $Cl_3MCo(CO)_3L_2$ were obtained for M = Sn and Ge and L = $P(n\text{-}C_4H_9)_3$ and $P(C_6H_5)_3$. They are formulated as ionic, $MCl_3^-[Co(CO)_3L_2]^+$, on the basis of infrared spectral data, including comparison with the previously reported $[Co(CO)_3L_2]B(C_6H_5)_4$. Under different reaction conditions the monosubstituted compounds, $Cl_3MCo(CO)_3L$, adjudged to be the trans isomers on the basis of their infrared spectra and the ^{59}Co nuclear quadrupole resonance spectra, are obtained. The ^{59}Co nqr spectra are reported for a number of phosphine-substituted compounds.

Many five-coordinate cobalt tetracarbonyl compounds containing cobalt–metal bonds have been prepared in recent years. The characteristics of the metal–cobalt bond, particularly the extent of π bonding, have been discussed on the basis of molecular structure,[3–6] vibrational spectra,[7,8] and nuclear quadrupole resonance data.[9–12] However, the chemical behavior of these compounds has not been fully studied. In the present publication, we report an investigation of the reactions of $Cl_3MCo(CO)_4$ (M = Sn, Ge, Si) systems with nucleophiles such as $P(n\text{-}C_4H_9)_3$, $P(C_6H_5)_3$, and $P(OC_2H_5)_3$. The initial intent of the work was to determine the effect of the Cl_3M group on the kinetics of CO substitution. It soon became apparent, however, that the reactions were not simple substitutions.

The reactivities of $R_3SiCo(CO)_4$ (R = H, CH_3, Cl) compounds with some bases have been described.[13] In the presence of trimethylamine or trimethylphosphine $R_3SiCo(CO)_4$ (R = H and CH_3) undergo heterolytic cleavage of the Si–Co bond to produce $[R_3SiB]^+[Co(CO)_4]^-$.[13,14] Substitutions on cobalt by the reaction of $P(C_6H_5)_3$ with $H_3SiCo(CO)_4$[15] and $P(C_2H_5)_3$ with $R_3SiCo(CO)_4$(R = C_2H_5 and Cl)[16] have been reported.

The reactions of $Co_2(CO)_8$ with bases have been ex-

---

[1] This research was supported through Grant 6396 X from the National Science Foundation.

[2] On leave from Department of Chemistry, Tohoku University, Sendai, Japan.

[3] W. T. Robinson and J. A. Ibers, *Inorg. Chem.*, **6**, 1208 (1967).

[4] A. G. Robiette, G. M. Sheldrick, R. N. F. Simpson, B. J. Aylett, and J. M. Campbell, *J. Organometal. Chem.*, **14**, 279 (1968).

[5] K. Emerson, P. R. Ireland, and W. T. Robinson, *Inorg. Chem.*, **9**, 436 (1970).

[6] J. K. Stalick and J. A. Ibers, *J. Organometal. Chem.*, **22**, 213 (1970).

[7] D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, **6**, 981 (1967).

[8] K. L. Watters, J. N. Brittain, and W. M. Risen, Jr., *ibid.*, **8**, 1347 (1969).

[9] T. L. Brown, P. A. Edwards, C. B. Harris, and J. L. Kirsch, *ibid.*, **8**, 763 (1969).

[10] A. N. Nesmeyanov, G. K. Semin, E. V. Bryuchova, K. N. Anisimov, N. E. Kolobova, and V. N. Khandozhko, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1936 (1969).

[11] D. D. Spencer, J. L. Kirsch, and T. L. Brown, *Inorg. Chem.*, **9**, 235 (1970).

[12] J. D. Graybeal, S. D. Ing, and M. W. Hsu, *ibid.*, **9**, 678 (1970).

[13] J. F. Bald, Jr., and A. G. MacDiarmid, *J. Organometal. Chem.*, **22**, C22 (1970).

[14] B. J. Aylett and J. M. Campbell, *J. Chem. Soc. A*, 1920 (1969).

[15] B. J. Aylett and J. M. Campbell, *ibid.*, 1910 (1969).

[16] O. Kahn and M. Bigorgne, *J. Organometal. Chem.*, **10**, 137 (1967).