for the isocyanate complex than for the analogous chloride (CCl₄ 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

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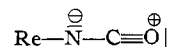
which places a high electron density on the N atom. This negative charge may then be donated to the Re to replace the electron density which is removed by the departing CO group. The entropy of activation (+1.8 eu) is somewhat low yet is in the range commonly found[18] for CO dissociation in other metal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

Reactions of Cl₃MCo(CO)₄ Compounds with Lewis Bases[1]

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

The reactions of Cl₃MCo(CO)₄ (M = Si, Ge, Sn) compounds with P(OC₂H₅)₃, P(n-C₄H₉)₃, and P(C₆H₅)₃ have been studied. Reaction of Cl₃SnCo(CO)₄ with P(OC₂H₅)₃, P(n-C₄H₉)₃, or N(C₂H₅)₃ in hexane or with THF in the neat solvent leads to formation of SnCl₂[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 Cl₃SnCo(CO)₄ by Co(CO)₄⁻. In the presence of excess base, products of the form Cl₃MCo(CO)₃L₂ were obtained for M = Sn and Ge and L = P(n-C₄H₉)₃ and P(C₆H₅)₃. They are formulated as ionic, MCl₃⁻[Co(CO)₃L₂]⁺, on the basis of infrared spectral data, including comparison with the previously reported [Co(CO)₃L₂]B-(C₆H₅)₄. Under different reaction conditions the monosubstituted compounds, Cl₃MCo(CO)₃L, adjudged to be the trans isomers on the basis of their infrared spectra and the ⁵⁹Co nuclear quadrupole resonance spectra, are obtained. The ⁵⁹Co 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 Cl₃MCo(CO)₄ (M = Sn, Ge, Si) systems with nucleophiles such as P(n-C₄H₉)₃, P(C₆H₅)₃, and P(OC₂H₅)₃. The initial intent of the work was to determine the effect of the Cl₃M group on the kinetics of CO substitution. It soon became apparent, however, that the reactions were not simple substitutions.

The reactivities of R₃SiCo(CO)₄ (R = H, CH₃, Cl) compounds with some bases have been described.[13] In the presence of trimethylamine or trimethylphosphine R₃SiCo(CO)₄ (R = H and CH₃) undergo heterolytic cleavage of the Si–Co bond to produce [R₃SiB]⁺-[Co(CO)₄]⁻.[13,14] Substitutions on cobalt by the reaction of P(C₆H₅)₃ with H₃SiCo(CO)₄[15] and P(C₂H₅)₃ with R₃SiCo(CO)₄(R = C₂H₅ and Cl)[16] have been reported.

The reactions of Co₂(CO)₈ with bases have been ex-

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(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. P. 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).

TABLE I
ANALYSES (%)

	C		H		Cl		Co	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$Cl_3SiCoP(n-C_4H_9)_3(CO)_3$	37.56	37.82	5.68	5.67	12.28	12.38		
$Cl_3GeCoP(n-C_4H_9)_3(CO)_3$	34.37	34.66	5.19	5.14	20.28	20.18	11.24	11.16
$Cl_3SnCoP(n-C_4H_9)_3(CO)_3$	31.59	31.45	4.77	4.96	18.65	18.57	10.33	10.25
$Cl_3SnCo[P(n-C_4H_9)_3]_2(CO)_3$	41.97	42.34	7.05	6.96	13.77	13.27		
$Cl_3GeCoP(C_6H_5)_3(CO)_3$	43.17	43.49	2.59	2.64	18.21	17.34	10.09	9.88
$Cl_3GeCo[P(C_6H_5)_3]_2(CO)_3$	55.35	55.51	3.57	3.56				
$Cl_3SnCo[P(C_6H_5)_3]_2(CO)_3$	52.48	52.53	3.39	3.49	11.92	11.93	6.60	6.75
$Cl_3GeCoAs(C_6H_5)_3(CO)_3$	40.15	40.47	2.41	2.50	16.93	16.81		
$Cl_3SnCoAs(C_6H_5)_3(CO)_3$	37.41	37.69	2.24	2.10	15.77	15.73		
$[Co[P(n-C_4H_9)_3]_2(CO)_3^+][B(C_6H_5)_4^-]$	70.67	70.39	8.61	8.53			6.80	7.04

							Sn	
							Calcd	Found
$(C_2H_5)_4NSnCl_3$	27.04	26.52	5.67	5.53	29.93	29.41	33.40	32.85
$KSnCl_3$					40.27	40.05	44.93	45.13

tensively investigated. These reactions often result in heterolytic cleavage of the Co–Co bond

$$Co_2(CO)_8 + 2L \longrightarrow CoL_2(CO)_3^+ + Co(CO)_4^- \quad (1)$$
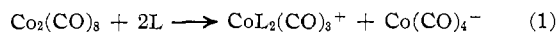
where L may be $P(C_6H_5)_3$,[17] $P(n-C_4H_9)_3$,[18] $P[N-(CH_3)_2]_3$,[19] etc. Alternatively, with these bases and with some phosphites[20,21] simple CO substitution may occur, as in

$$Co_2(CO)_8 + 2L \longrightarrow Co_2(CO)_6L_2 + 2CO \quad (2)$$

or

$$Co_2(CO)_8 + L \longrightarrow Co_2(CO)_7L + CO \quad (3)$$
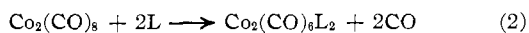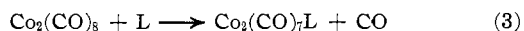
We have found that nucleophilic attack on $Cl_3MCo(CO)_4$ may result in displacement of CO, in coordination at Co, or in heterolytic rupture of the M–Co bond to produce $[MCl_3L_n]^+[Co(CO)_4]^-$ or $MCl_3^-[CoL_n(CO)_{5-n}]^+$.

Experimental Section

$Cl_3SnCo(CO)_4$,[22] $Cl_3GeCo(CO)_4$,[7] and $Cl_3SiCo(CO)_4$[23] were prepared according to methods described in the literature. $Cl_3SnCo(CO)_4$ was also prepared by treating $(C_6H_5)_3SnCo(CO)_4$ with excess $SnCl_4$. The $Cl_3SnCo(CO)_4$ formed was recrystallized from *n*-hexane. This method yielded 7 g of $Cl_3SnCo(CO)_4$ from 5 g of $Co_2(CO)_8$.

Reactions between the carbonyl compounds and bases were carried out under an argon atmosphere. In addition, kinetic studies were carried out in the dark.

$Cl_3SiCoP(n-C_4H_9)_3(CO)_3$.—When 0.165 g of $P(n-C_4H_9)_3$ (0.82 mmol) in 10 ml of *n*-hexane was added to 0.25 g of $Cl_3SiCo(CO)_4$ (0.82 mmol) in 10 ml of *n*-hexane, some turbidity was observed. The solution was filtered and the filtrate was concentrated to 3 ml under reduced pressure, affording yellow crystals; yield 0.18 g.

$Cl_3GeCoP(n-C_4H_9)_3(CO)_3$.—A 0.05-g sample of $P(n-C_4H_9)_3$ (0.25 mmol) in 2 ml of benzene was added to 0.09 g of $Cl_3GeCo(CO)_4$ (0.26 mmol) in 5 ml of benzene and 5 ml of THF. After 20 min solvent volume was reduced to 3 ml; the crystals formed were washed with *n*-hexane; yield 0.05 g. This compound was also obtained in 80% yield by adding $Cl_3GeCo(CO)_4$ to a slight excess of $P(n-C_4H_9)_3$ without solvent. The product was washed with small amounts of benzene and thoroughly washed with *n*-hexane.

$Cl_3GeCoP(C_6H_5)_3(CO_3)$ and $Cl_3GeCo[P(C_6H_5)_3]_2(CO)_3$.—A 1.15-g sample of $P(C_6H_5)_3$ (4.4 mmol) in 100 ml of benzene was added to 1.66 g of $Cl_3GeCo(CO)_4$ (4.7 mmol) in 100 ml of benzene. After 1 hr, the solution was filtered, affording 0.35 g of yellow precipitate of composition $Cl_3GeCo[P(C_6H_5)_3]_2(CO)_3$. The filtrate was concentrated to ~5 ml. Addition of *n*-hexane afforded 1.7 g of yellow precipitate of a composition corresponding to $Cl_3GeCoP(C_6H_5)_3(CO)_3$.

$Cl_3GeCoAs(C_6H_5)_3(CO)_3$.—A 0.05-g sample of $Cl_3GeCo(CO)_4$ (0.14 mmol) and 0.05 g of $As(C_6H_5)_3$ (0.16 mmol) were mixed in 10 ml of *n*-hexane. After 1 hr, the solvent was removed under reduced pressure until yellow crystals appeared; these were washed with a small amount of *n*-hexane; yield 0.06 g.

$Cl_3SnCoP(n-C_4H_9)_3(CO)_3$.[24]—(a) A 1.25 g sample of $Cl_3SnCo(CO)_4$ (3.1 mmol) in 40 ml of benzene was added dropwise to 0.65 g of $P(n-C_4H_9)_3$ (3.2 mmol) in 60 ml of benzene. After 1 hr the solution was filtered and the yellow precipitate was washed with benzene; yield 1.4 g. (b) A 0.05-g sample of $Cl_3SnCo(CO)_4$ (0.13 mmol) in 10 ml of benzene was added to 0.10 g of $Cl_3SnCo[P(n-C_4H_9)_3]_2(CO)_3$ (0.13 mmol) in 10 ml of benzene. The resulting precipitate was washed with benzene; yield 0.14 g.

$Cl_3SnCo[P(n-C_4H_9)_3]_2(CO)_3$.—A 0.06-g sample of $P(n-C_4H_9)_3$ (0.3 mmol) was added to 0.06 g of $Cl_3SnCo(CO)_4$ (0.15 mmol) in 20 ml of *n*-hexane. The resulting yellow precipitate was recrystallized by dissolving in benzene followed by the addition of *n*-hexane; yield 0.07 g.

$Cl_3SnCo[P(C_6H_5)_3]_2(CO)_3$.—A 0.08-g sample of $P(C_6H_5)_3$ (0.3 mmol) in 3 ml of *n*-hexane was added to 0.06 g of $Cl_3SnCo(CO)_4$ (0.15 mmol) in 10 ml of *n*-hexane. A 0.13-g amount of yellow precipitate was obtained.

$Cl_3SnCoAs(C_6H_5)_3(CO)_3$.—A 0.05-g sample of $Cl_3SnCo(CO)_4$ (0.13 mmol) in 10 ml of *n*-hexane was added to 0.11 g of $As(C_6H_5)_3$ (0.33 mmol) in 10 ml of *n*-hexane. After 1 hr, the solution was filtered and a yellow precipitate was extracted with benzene. The benzene solution was concentrated under reduced pressure. Addition of *n*-hexane afforded 0.02 g of $Cl_3SnCoAs(C_6H_5)_3(CO)_3$.

$[Co[P(n-C_4H_9)_3]_2(CO)_3]B(C_6H_5)_4$.—An excess of $NaB(C_6H_5)_4$ was added to an acetone solution of $Cl_3SnCo[P(n-C_4H_9)_3]_2(CO)_3$. Addition of water afforded a colorless precipitate of $Co[P(n-C_4H_9)_3]_2(CO)_3B(C_6H_5)_4$. $Co[P(C_6H_5)_3]_2(CO)_3B(C_6H_5)_4$[25] was obtained in the same manner from $Cl_3SnCo[P(C_6H_5)_3]_2(CO)_3$.

$(C_2H_5)_4NSnCl_3$ was prepared by mixing $SnCl_2$ and $(C_2H_5)_4NCl$ in ethanol. $KSnCl_3 \cdot H_2O$ was obtained by mixing equimolar $SnCl_2$ and KCl in a small amount of water. The anhydrous material was obtained by drying under vacuum for 24 hr.

Analytical data for the above compounds are given in Table I. Table II lists the CO infrared stretching frequencies obtained

(17) W. Hieber and W. Freyer, *Chem. Ber.*, **91**, 1230 (1958).

(18) F. Piacenti, M. Bianchi, and E. Benedetti, *Chim. Ind. (Milan)*, **49**, 245 (1967).

(19) R. B. King, *Inorg. Chem.*, **2**, 936 (1963).

(20) A. Sacco, *Ann. Chim. (Rome)*, **43**, 495 (1953).

(21) P. Szabo, L. Fekete, and G. Bor, *J. Organometal. Chem.*, **12**, 245 (1968).

(22) D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, **7**, 771 (1968).

(23) D. Darensbourg, Ph.D. Thesis, University of Illinois, 1968.

(24) This compound was prepared by the reaction $Co(CO)_3P(n-C_4H_9)_3$-$HgCl + SnCl_2 \rightarrow Cl_3SnCoP(n-C_4H_9)_3(CO)_3$: F. Bonati, S. Cenini, and R. Ugo, *J. Chem. Soc. A*, 932 (1967).

(25) This compound was prepared by Hieber and Freyer[17] by a different method. A trans structure was proposed for the cation $Co[P(C_6H_5)_3]_2(CO)_3^+$: O. Vohler, *Chem. Ber.*, **91**, 1235 (1958).

<div align="center">TABLE II</div>

<div align="center">INFRARED DATA FOR $Cl_3MCoL_n(CO)_3$ COMPOUNDS (CM^{-1})</div>

	ν(C–O) in CHCl₃ soln	600–250 cm⁻¹ (in Nujol mull)[b]	ν(Sn–Cl)or ν(Ge–Cl)
	1983 s[a]		
$Cl_3SiCoP(n-C_4H_9)_3(CO)_3$	2052 vw, 1980 s, 1987 s	576 s, 550 s, sh, 547 s, 494 s, sh, 486 m, sh	
$Cl_3GeCoP(n-C_4H_9)_3(CO)_3$	2064 vw, 1993 s, 2002 s	572 s, 560 s, 510 m, 497 m, 487.5 s	376 s, 366 s
$Cl_3SnCoP(n-C_4H_9)_3(CO)_3$	2060 vw, 1995 s	577 s, 555 s, 511 m, 498 m, 485 s	338 s
$Cl_3SnCo[P(n-C_4H_9)_3]_2(CO)_3$	2066 vw, 1990 s, 1995 s 2003 s[a]	575 s, 557 w, 516 m, 500 s	296 m, 292 m
$Cl_3GeCoAs(C_6H_5)_3(CO)_3$	2064 vw, 2004 s 2000 s[a]	561 s, 505 w, 482 s, 475 m, 468 m	390 sh, 379 s
$Cl_3SnCoAs(C_6H_5)_3(CO)_3$	2061 vw, 2003 s 2004 s[a]	557 s, 500 w, 481 s, 474 m, 468 m	351 s, 343 s, 337 sh
$Cl_3GeCoP(C_6H_5)_3(CO)_3$	2065 vw, 2004 s	560 s, 523 s, 481 s, 471 w, sh	386 s, sh, 379 s
$Cl_3GeCo[P(C_6H_5)_3]_2(CO)_3$	2074 vw, 2005 s, 2011 s	563 s, 523 s, 514 s, 477 w, sh, 472 m	335 m, 294 m, 275 w
$Cl_3SnCo[P(C_6H_5)_3]_2(CO)_3$	2075 vw, 2006 s, 2012 s	563 s, 523 s, 513 s, 477 m, 472 m, sh	294 m
$Co[P(C_6H_5)_3]_2(CO)_3B(C_6H_5)_4$	2074 vw, 2006 s, 2012 s	563 s, 523 s, 513 s, 477 w, sh, 472 m	
$(C_2H_5)_4NSnCl_3$			298, 279
$KSnCl_3$			~310

[a] In n-hexane; because of limited solubility, the low-intensity band at higher frequency was not obtained.   [b] ν(Co–C), δ(Co–C–O), ν(Si–Cl), or bands due to L.

with a frequency-calibrated Beckman IR 7 and bands seen in the 600–250-cm⁻¹ region, measured with a frequency-calibrated Beckman IR 20A. Infrared spectra of $Cl_3MCo(CO)_4$ (M = Sn, Ge, Si) have recently been reported.[6]

Reaction between $Cl_3SnCo(CO)_4$ and $P(OC_2H_5)_3$.—A 0.50-g sample of $Cl_3SnCo(CO)_4$ (0.125 mmol) in 10 ml of n-hexane was mixed with 0.0166 g of $P(OC_2H_5)_3$ (0.10 mmol) in 5 ml of n-hexane, and the solution was kept at 40°. After 24 hr the reaction was complete; the infrared spectrum of the solution showed that it contained $Cl_3SnCo(CO)_4$ and $Cl_2Sn[Co(CO)_4]_2$[7] in a molar ratio of 6:10. The solution was filtered leaving an oily residue. The filtrate was evaporated and cooled in Dry Ice. Orange-yellow crystals obtained were identified as $Cl_2Sn[Co(CO)_4]_2$ on the basis of the infrared spectrum,[7] melting point,[26] and analysis. *Anal.* Calcd for $Cl_2Sn[Co(CO)_4]_2$: C, 18.04. Found: C, 18.52. The oily residue was dissolved in benzene. On the addition of pyridine to this solution a precipitate formed; it was identified as $SnCl_4(C_5H_5N)_2$ from its infrared spectrum.[27]

The kinetic behavior of this reaction was studied. Since it was found to be light sensitive, kinetic runs were carried out in a completely dark vessel fitted with a rubber serum cap. n-Hexane solutions of $Cl_3SnCo(CO)_4$ and $P(OC_2H_5)_3$ were kept in a thermostated bath at 30.0°. $P(OC_2H_5)_3$ solution was injected into the $Cl_3SnCo(CO)_4$ solution. At appropriate time intervals portions of the solution were withdrawn and placed in a 1-mm path length sodium chloride cell and the infrared spectra were recorded. A specially constructed cell chamber was kept at 30° with a flow of thermostated air. All visible light to the cell was cut off by means of a Kodak Series 200 S filter.

Nuclear quadrupole resonance spectra were obtained as described previously.[11]

Results and Discussion

Reaction between $Cl_3SnCo(CO)_4$ and $P(OC_2H_5)_3$.— Figure 1 shows the change with time in the infrared spectrum of 7×10^{-4} M $Cl_3SnCo(CO)_4$ and 0.026 M $P(OC_2H_5)_3$ in n-hexane. The spectra show isosbestic points at frequencies at which $Cl_3SnCo(CO)_4$ and $Cl_2Sn[Co(CO)_4]_2$ have the same extinction coefficients. It therefore appears that there is no stable intermediate produced in the reaction, and the overall process can be expressed as

$$2Cl_3SnCo(CO)_4 + nP(OC_2H_5)_3 \longrightarrow Cl_2Sn[Co(CO)_4]_2 + SnCl_4[P(OC_2H_5)_3]_n \quad (4)$$
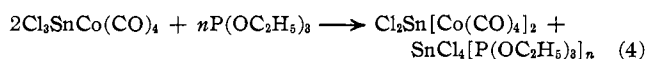
(26) D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, **5**, 1405 (1966).

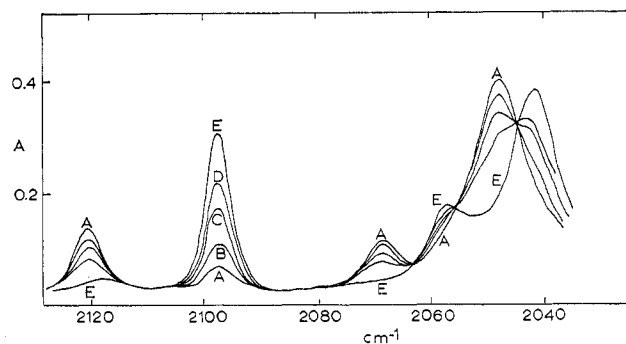(27) I. R. Beattie, G. P. McQuillan, L. Rule, and M. Webster, *J. Chem. Soc.*, 1514 (1963).

Figure 1.—Infrared spectra of a hexane solution containing 0.026 M $P(OC_2H_5)_3$ and 7×10^{-4} M $Cl_3SnCo(CO)_4$, at various times: A, 5 min; B, 21 min; C, 37 min; D, 48 min; E, 97 min.
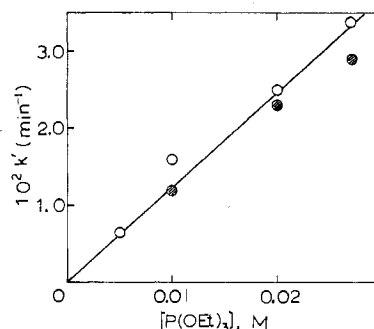

Figure 2.—Pseudo-first-order rate constant k' as a function of $P(OC_2H_5)_3$ concentration, using the absorption at 2120.5 cm⁻¹ (O) and at 2097.5 cm⁻¹ (●).

A reaction mixture initially containing 0.125 mmol of $Cl_3SnCo(CO)_4$ and 0.1 mmol of $P(OC_2H_5)_3$ was found to contain $Cl_3SnCo(CO)_4$ and $Cl_2Sn[Co(CO)_4]_2$ in about a 6:10 molar ratio, upon completion of the reaction, indicating that n in eq 4 is probably 2.

From log $|A\infty - A|$ *vs.* t plots it was ascertained that the reaction obeyed pseudo-first-order kinetics. The pseudo-first-order rate constant k' was obtained and is displayed in Figure 2 as a function of the phosphite concentration. These results indicate that the rate expression is

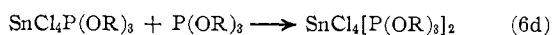$$\text{rate} = k[Cl_3SnCo(CO)_4][P(OC_2H_5)_3] \quad (5)$$

The values of k are given in Table III.

TABLE III
RATE OF REACTION 4 IN n-HEXANE AT 30°

10^3[Cl$_3$SnCo-(CO$_4$)], M	10^3[P(OC$_2$H$_5$)$_3$],	10^2k, min^{-1}	k, M^{-1} min^{-1}
0.51	5	0.65	1.3^a
0.51	10	1.6	1.6^a
0.51	10	1.2	1.2^a
0.51	20	2.5	1.3^a
0.51	20	2.3	1.1^b
0.55	27	3.4	1.2^b
0.28	27	2.9	1.1^b

^{a} Followed at 2120.5 cm^{-1}. ^{b} Followed at 2097.5 cm^{-1}.

The mechanism of reaction 4 is possibly

$$Cl_3SnCo(CO)_4 + P(OR)_3 \rightleftharpoons Cl_3SnCo(CO)_4P(OR)_3 \quad (6a)$$

$$Cl_3SnCo(CO)_4P(OR)_3 \longrightarrow [Co(CO)_4{}^-][Cl_3SnP(OR)_3{}^+] \quad (6b)$$

$$Cl_3SnCo(CO)_4 + [Co(CO)_4{}^-][Cl_3SnP(OR)_3{}^+] \longrightarrow$$
$$Cl_2Sn[Co(CO)_4]_2 + SnCl_4P(OR)_3 \quad (6c)$$

$$SnCl_4P(OR)_3 + P(OR)_3 \longrightarrow SnCl_4[P(OR)_3]_2 \quad (6d)$$
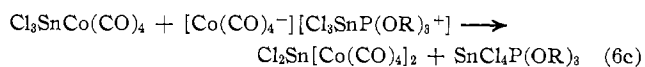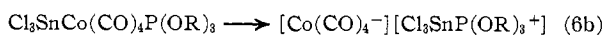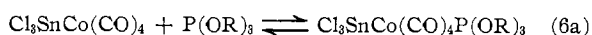
The species formed in step 6a is assumed to be a phosphite adduct of tin. The role of phosphite in the reaction can be considered to be production of Co(CO)$_4$$^-$ anion. It is not clear from the rate law at which stage of the reaction the second phosphite is involved. It is certain only that it is involved in a reaction subsequent to the rate-determining step. Formation of Co(CO)$_4$$^-$ has been observed in the reaction between R$_3$SiCo(CO)$_4$ and some bases.[13,14] The compound R$_3$SnCo(CO)$_4$ is considered to dissociate to R$_3$Sn$^+$ and Co(CO)$_4$$^-$ in acetone, methanol,[28] and DMF.[29] The rate-determining step is probably formation of Co(CO)$_4$$^-$. Adduct formation (step 6a) should be rapid but probably does not proceed far to the right (*vide infra*).

The dicobalt species Cl$_2$Sn[Co(CO)$_4$]$_2$ is formed rapidly when Cl$_3$SnCo(CO)$_4$ is dissolved in THF (half-time $\sim$30 min at room temperature) and in n-hexane solutions containing P(n-C$_4$H$_9$)$_3$ or N(C$_2$H$_5$)$_3$ at low concentration ($\sim$1 mM); reaction was complete within 5 min. These observations can also be understood in terms of the mechanism proposed. The steps corresponding to (6a) and (6b) are much more rapid with P(n-C$_4$H$_9$)$_3$ or N(C$_2$H$_5$)$_3$ than with P(OC$_2$H$_5$)$_3$ because P(n-C$_4$H$_9$)$_3$ and N(C$_2$H$_5$)$_3$ are stronger bases than P(OC$_2$H$_5$)$_3$ toward tin in Cl$_3$SnCo(CO)$_4$. When P(n-C$_4$H$_9$)$_3$ or N(C$_2$H$_5$)$_3$ are added in high concentrations to a Cl$_3$SnCo(CO)$_4$ solution in n-hexane, formation of Cl$_2$Sn[Co(CO)$_4$]$_2$ was not observed. Under these conditions, steps 6a and 6b proceed very rapidly compared to step 6c, and all Cl$_3$SnCo(CO)$_4$ is converted to the adduct; the Co(CO)$_4$$^-$ thus produced cannot react with Cl$_3$SnCo(CO)$_4$ to form Cl$_2$Sn[Co(CO)$_4$]$_2$. The compound Cl$_3$SnCo[P(n-C$_4$H$_9$)$_3$]$_2$(CO)$_3$ is formed in the case of P(n-C$_4$H$_9$)$_3$. The final product of the reaction between Cl$_3$SnCo(CO)$_4$ and N(C$_2$H$_5$)$_3$ was not identified.

Reaction 4 is similar to the reaction between Pt-(C$_5$H$_5$N)$_2$[Co(CO)$_4$]$_2$ and P(C$_6$H$_5$)$_3$ or P(n-C$_4$H$_9$)$_3$.[30]

(28) A. D. Beveridge and H. C. Clark, *J. Organometal. Chem.*, **11**, 601 (1968).
(29) J. M. Burtlitch, *J. Amer. Chem. Soc.*, **91**, 4562 (1969).
(30) R. G. Pearson and J. Dehand, *J. Organometal. Chem.*, **16**, 485 (1969).

in that cleavage of the Co–metal bond occurs instead of cleavage of the Co–CO bond.

Cl$_3$MCoL(CO)$_3$ and Cl$_3$MCoL$_2$(CO)$_3$.—These two types of phosphine- or arsine-substituted compounds were synthesized by mixing the corresponding carbonyl compound and base. The Cl$_3$MCoL(CO)$_3$ compounds are assigned the trans structure on the basis of the infrared CO spectra; the higher frequency band of very low intensity is the totally symmetric A$_1$ mode; the intense band at lower frequency is due to the E mode. The trans structure has been assigned to several cobalt carbonyl compounds on the basis of the CO stretching bands.[16,22] The very small or zero asymmetry parameter found in ^{59}Co nuclear quadrupole resonance spectra of Cl$_3$MCoL(CO)$_3$ compounds are also consistent with the trans structure.

In Cl$_3$MCoL$_2$(CO)$_3$ compounds, the number of carbonyl groups in the compound is not clear from the chemical analysis alone, because of the high molecular weight. However, the molar integrated intensity of the infrared CO stretching bands of Cl$_3$GeCo[P(C$_6$H$_5$)$_3$]$_2$(CO)$_3$ was found to be smaller than that of Cl$_3$GeCoP(C$_6$H$_5$)$_3$(CO)$_3$ by only about 8%. This suggests that the former compound has also three carbonyl groups, since the integrated intensity should be roughly proportional to the number of CO groups.

The CO stretching regions are similar in the ir spectra of Cl$_3$MCoL(CO)$_3$ and Cl$_3$MCoL$_2$(CO)$_3$. On the other hand, distinct differences in ir spectra of Cl$_3$MCoL-(CO)$_3$ and Cl$_3$MCoL$_2$(CO)$_3$ are observed at frequencies lower than 400 cm^{-1} (Table II). Bands in this region are considered to be due to Sn–Cl or Ge–Cl stretching. The M–Cl bands for Cl$_3$MCoL(CO)$_3$ have similar shapes and intensity to those for Cl$_3$MCo(CO)$_4$, while the M–Cl bands for Cl$_3$MCoL$_2$(CO)$_3$ are markedly different. The Sn–Cl stretching bands in Cl$_3$SnCoL$_2$(CO)$_3$ appear at frequencies close to those for SnCl$_3$$^-$ salts. The frequencies of the M–Cl modes for Cl$_3$MCoL(CO)$_3$ change with the nature of L in the order[8] CO > P(C$_6$H$_5$)$_3$ $\sim$ As(C$_6$H$_5$)$_3$ > P(n-C$_4$H$_9$)$_3$. The infrared spectra of Cl$_3$SnCo[P(C$_6$H$_5$)$_3$]$_2$(CO)$_3$, Cl$_3$GeCo[P-(C$_6$H$_5$)$_3$]$_2$(CO)$_3$, and Co[P(C$_6$H$_5$)$_3$]$_2$(CO)$_3$B(C$_6$H$_5$)$_4$ are essentially the same in the CO stretching and 600–400-cm^{-1} regions. From the above comparison of infrared spectra and the observation that the ionic species [CoL$_2$(CO)$_3$$^+$][B(C$_6H_5$)$_4$$^-$] was obtained by the reaction of Cl$_3$SnCoL$_2$(CO)$_3$ and NaB(C$_6$H$_5$)$_4$, an ionic structure [*trans*-CoL$_2$(CO)$_3$$^+$][MCl$_3$$^-$] is proposed for Cl$_3$MCoL$_2$-(CO)$_3$ compounds. The intense CO stretching band at $\sim$2000 cm^{-1} is assigned as the E species mode. The very low intensity band at higher frequency is the nearly infrared-inactive A$_1$ mode absorption.

Cl$_3$MCoL(CO)$_3$ compounds are less reactive toward substitution than Cl$_3$MCo(CO)$_4$. Cl$_3$SiCoP(n-C$_4$H$_9$)$_3$-(CO)$_3$ and Cl$_3$GeCoP(n-C$_4$H$_9$)$_3$(CO)$_3$ are stable in neat P(n-C$_4$H$_9$)$_3$, whereas the corresponding tetracarbonyls react immediately. The THF solution of Cl$_3$SnCoP-(n-C$_4$H$_9$)$_3$(CO)$_3$ did not show formation of species such as Cl$_2$Sn[CoP(n-C$_4$H$_9$)$_3$(CO)$_3$]$_2$ after 24 hr, presumably because the activation energy for reactions such as

(6a) and (6b) is larger for Cl₃SnCoL(CO)₃ than for Cl₃SnCo(CO)₄. This corresponds to the result that the pK_a of HCoL(CO)₃ is considerably higher for L = P(C₆H₅)₃ than for L = CO[31,32] and adds further support to the proposed mechanism. The rate in the slow step should be related to the relative ability of the cobalt-containing species to act as a leaving group.

It was found that Cl₃GeCoP(C₆H₅)₃(CO)₃ was stable in benzene solution containing P(C₆H₅)₃ or in neat P(*n*-C₄H₉)₃. This indicates that Cl₃GeCoP(C₆H₅)₃-(CO)₃ is not an intermediate in the formation of Cl₃-GeCo[P(C₆H₅)₃]₂(CO)₃. The mechanisms of formation of two types of phosphine-substituted compounds are not clear at this stage. The reaction between RCOCo-(CO)₄ and P(C₆H₅)₃ to form RCOCoP(C₆H₅)₃(CO)₃[33] and the CO exchange reaction of RCOCo(CO)₄[34] were reported to proceed *via* a dissociative mechanism. On the other hand, the formation of Cl₃MCoL(CO)₃ from Cl₃MCo(CO)₄ and L cannot proceed *via* a simple dissociative mechanism, because the ¹³CO exchange reaction of Cl₃GeCo(CO)₄ is much slower.[35] It does appear, however, that both the acidity of M in Cl₃-MCo(CO)₄ and the basicity of L are important factors in the reaction.

The formation of two types of compounds, [CoL₂-(CO)₃⁺][MCl₃⁻] and Cl₃MCoL(CO)₃, corresponds to reactions of Co₂(CO)₈ with phosphines, expressed by eq 1 and 2. The relative amounts of the two compounds depend on the conditions, especially solvent and concentration. The ionic compound Cl₃SnCo-[P(*n*-C₄H₉)₃]₂(CO)₃ was found to react with Cl₃SnCo-(CO)₄ in benzene to yield Cl₃SnCoP(*n*-C₄H₉)₃(CO)₃ (and Cl₃GeCo[P(C₆H₅)₃]₂(CO)₃ with Cl₃GeCo(CO)₄ in 1:1 benzene–THF solution to give Cl₃GeCoP(C₆H₅)₃-(CO)₃) according to

$$[CoL_2(CO)_3{}^+][MCl_3{}^-] + Cl_3MCo(CO)_4 \longrightarrow$$
$$2Cl_3MCoL(CO)_3 + CO \quad (7)$$
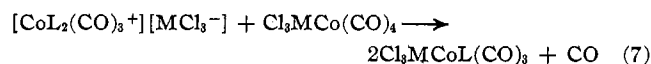
This reaction corresponds to that of the derivative of Co₂(CO)₈[18,36]

$$[CoL_2(CO)_3{}^+][Co(CO)_4{}^-] \longrightarrow [CoL(CO)_3]_2 + CO \quad (8)$$
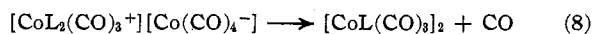
Some reactions of Cl₃MCo(CO)₄ with bases can thus be closely related to those of Co₂(CO)₈ in which the Cl₃M group is replaced by a (CO)₄Co group.

Nuclear Quadrupole Resonance Spectra.—The ⁵⁹Co and ³⁵Cl nuclear quadrupole resonance spectra were obtained for a number of phosphine-substituted compounds. The results are given in Table IV. Axial substitution of the trichlorotin and trichlorogermanium compounds by either triphenylphosphine or tributylphosphine results in only a small change in eQq at cobalt. Nesmeyanov and coworkers[10] have reported analogous data for the triphenylphosphine-substituted trichlorotin compound at 77°K. The temperature coefficient of the ⁵⁹Co quadrupole coupling constant is

(31) W. Hieber and E. Lindner, *Z. Naturforsch. B*, **16**, 137 (1961).
(32) W. Hieber and E. Lindner, *Chem. Ber.*, **94**, 1417 (1961).
(33) F. Heck, *J. Amer. Chem. Soc.*, **85**, 651 (1963).
(34) S. Breitschaft and F. Basolo, *ibid.*, **88**, 2702 (1966).
(35) R. S. Gay and W. A. G. Graham, personal communication.
(36) J. A. McCleverty, A. Davison, and G. Wilkinson, *J. Chem. Soc.*, 3890 (1965).

TABLE IV
⁵⁹Co AND ³⁵Cl NUCLEAR QUADRUPOLE RESONANCE DATA (25°)

Compound	ν_2, MHz	ν_3, MHz	eQq	η	ν(³⁵Cl), MHz
Cl₃SiCo(CO)₄[a]	18.50	27.96	130.7	0.13	19.08
Cl₃SiCo(CO)₃P(*n*-C₄H₉)₃	16.27	24.40	113.9	0	...
Cl₃GeCo(CO)₄[a]	23.09	34.62	161.6	0	21.98[b]
	22.77	34.15	159.3		
Cl₃GeCo(CO)₃P(*n*-C₄H₉)₃	23.71	35.56	166.0	0	19.515
Cl₃GeCo(CO)₃P(C₆H₅)₃	22.31	33.58	156.9	0.08	...
	22.32	33.60	156.8	0.08	
Cl₃SnCo(CO)₄ [a]	23.38	35.02	163.4	0	19.880
Cl₃SnCo(CO)₃P(*n*-C₄H₉)₃	24.80	37.19	173.6	0	19.31
[Co(CO)₄][Co(CO)₃[P(C₆H₅)₃]₂]	22.77	34.20	159.7	0.05	...
[Co(CO)₃P(C₆H₅)₃]₂[c]	20.96	31.46	146.8	0	...

[a] Data from ref 9   [b] Average of three very closely spaced resonances: H. W. Spiess and R. K. Sheline, *J. Chem. Phys.*, **53**, 3036 (1970).   [c] Prepared as described in ref 36.

negative for the trichloro compounds, such that the coupling constant at room temperature is about 2–3 MHz lower than at 77°K.[9,10] We may therefore estimate from the Russian data that eQq for SnCl₃Co(CO)₃-P(C₆H₅)₃ at 25° is on the order of 160 MHz. Thus, in both the SnCl₃ and GeCl₃ compounds, axial substitution by P(C₆H₅)₃ results in a slight lowering of eQq, whereas axial substitution by P(*n*-C₄H₉)₃ results in a somewhat larger increase. By contrast, axial substitution on SiCl₃Co(CO)₄ by P(*n*-C₄H₉)₃ results in a substantial decrease in eQq. Unfortunately, the ³⁵Cl resonance in SiCl₃Co(CO)₃P(*n*-C₄H₉)₃ could not be seen.

On the basis of these limited data it appears that axial substitution does not markedly change the quadrupole coupling constant at Co when both axial ligands are capable of π-acceptor character. This generalization is exemplified also by the value of eQq for Co(CO)₃-[P(C₆H₅)₃]₂⁺, which can be thought of as derived from either Cl₃SnCo(CO)₃P(C₆H₅)₃ or Cl₃GeCo(CO)₃P-(C₆H₅)₃ by replacement of SnCl₃⁻ or GeCl₃⁻, respectively, by the neutral P(C₆H₅)₃.

In this connection, it is significant that the quadrupole coupling constant at Fe in Fe(CO)₄P(C₆H₅)₃ is essentially identical with that for Fe(CO)₅, as evidenced by the quadrupole splitting in the Mössbauer spectrum.[37] Similarly, the quadrupole coupling constant in Fe(CO)₄P(OC₂H₅)₃ is only slightly lowered from the value for the parent compound.[34]

The substituted binuclear compound [Co(CO)₃P-(C₆H₅)₃]₂ containing a Co–Co bond can be thought of as resulting from removal of the trichlorometal group from Cl₃GeCo(CO)₃P(C₆H₅)₃ or Cl₃SnCo(CO)₃P(C₆H₅)₃ and replacement by Co(CO)₃P(C₆H₅)₃.

The replacing ligand in this instance is not capable of π-acceptor action, however, and the quadrupole coupling constant decreases.

The asymmetry parameter is zero or nearly so in all of the substituted compounds examined. This is in agreement with the infrared evidence based on the CO stretching bands, which indicates trans substitution. The fact that η is zero for [Co(CO)₃P(C₆H₅)₃]₂ is evidence that the structure of this compound is similar to that of [Co(CO)₃P(*n*-C₄H₉)₃]₂, in which there are no bridging carbonyls.[38]

(37) R. L. Collins and R. Petit, *J. Chem. Phys.*, **39**, 3433 (1963).
(38) J. A. Ibers, *J. Organometal. Chem.*, **14**, 423 (1968).