TABLE III

PSEUDO-FIRST-ORDER RATE CONSTANTS IN NEUTRAL AND ACIDIC SOLUTIONS AT VARIOUS TEMPERATURES[a]

| In neutral soln[b] |  | In acidic soln[c] |  |  |  |
|---|---|---|---|---|---|
| Temp, °C | $10^5 k_0$, $sec^{-1}$ | $[HClO_4]$, *M* | 25° $10^4 k_{obsd}$, $sec^{-1}$ | 35° $10^4 k_{obsd}$, $sec^{-1}$ | 40° $10^3 k_{obsd}$, $sec^{-1}$ |
| 25.0 | 0.90 | 0.0453 | 2.0 | 6.4 | 1.1 |
| 39.5 | 6.4 | 0.136 | 5.2 | 17 | 3.0 |
| 49.7 | 19 | 0.226 | 8.3 | 28 | 4.8 |
| 59.7 | 59 | 0.317 | 11 | 37 | 6.7 |
|  |  | 0.453 | 16 | 54 | 9.4 |

[a] $[Co(tren)F_2]^+ = 3.0 \times 10^{-3}$ *M*. [b] No $HClO_4$ or $NaClO_4$ was added. [c] Ionic strength of reaction medium (0.5 *M*) maintained with $NaClO_4$.

For the acid-independent path ($k_0$), the activation parameters are $\Delta H^{\ddagger} = 22.3 \pm 0.6$ kcal $mol^{-1}$ and $\Delta S^{\ddagger} = -6.5 \pm 2$ cal $deg^{-1}$ $mol^{-1}$, while for the acid-catalyzed path ($k_H K_{eq}$), the parameters are $\Delta H^{\ddagger} = 21.0 \pm 0.3$ kcal $mol^{-1}$ and $\Delta S^{\ddagger} = 2.3 \pm 1.0$ cal $deg^{-1}$ $mol^{-1}$.

In the neutral solution, it was found that the acid hydrolysis reaction rate of $Co(tren)F_2^+$ ion at 25.0° ($9.0 \times 10^{-6}$ $sec^{-1}$) was about three times greater than that of *cis*-$Co(en)_2F_2^+$ ion ($3.06 \times 10^{-6}$ $sec^{-1}$).[7] Previous studies[3a,b] have indicated that the greater rates of acid hydrolysis of dichloro- and dibromo(triaminotriethylamine)cobalt(III) ions, as compared with the rates of corresponding complexes of bis(ethylenediamine), are due to steric strain produced by the peculiar geometry of the tren complex. The same conclusion may be drawn with regard to the $Co(tren)F_2^+$ ion. The positive intercept at zero hydrogen ion concentration in the plot of $k_{obsd}$ *vs.* $[H^+]$ is due to the contribution from the acid-independent pathway to the overall rate. However, only a one-term rate law

$$k_{obsd} = k_H K_{eq}[H^+] \qquad (7)$$

was found for the acid hydrolysis reaction in acidic solution of other fluoro-containing amminecobalt(III) complexes,[8,9] where the acid-independent pathway is not significant.

On comparison of the acid-independent acid hydrolysis reaction rate of $Co(tren)F_2^+$ ion at 25.0° to those of $Co(tren)Cl_2^+$ [3a] and $Co(tren)Br_2^+$ [3b] ions ($2.96 \times 10^{-3}$ and $2.81 \times 10^{-2}$ $sec^{-1}$, respectively), it is observed that the rate increases in the order F < Cl < Br. This was also observed for other haloamminecobalt(III) complexes.[8,9] The faster rate observed for the acid-catalyzed reaction is due to a weakening of the Co–F bond as a result of hydrogen bonding to form Co–FH.

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# Kinetics and Mechanism of the Reactions of Di-μ-carbonyl-bis(cyclopentadienyl)dinickel(0) with Monodentate Ligands

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The ligands carbon monoxide, triphenylarsine, triphenyl phosphite, triphenylphosphine, ethyldiphenylphosphine, and tri-*n*-butylphosphine react with di-μ-carbonyl-bis(cyclopentadienyl)dinickel(0) to give nickelocene and diliganddicarbonylnickel(0) (eq 1). The kinetics of these reactions have been studied by following the carbonyl region infrared spectra of reaction mixtures or by manometric observation of carbon monoxide absorption. Complicated behavior is observed with tri-*n*-butylphosphine. The dependence on carbon monoxide concentration was not studied, but reaction according to (1) is much slower than the rate reported for carbon monoxide exchange. For the other ligands studied, a second-order rate law, first order in each reactant, is observed: $-d[Ni_2(CO)_2(C_5H_5)_2]/dt = k[Ni_2(CO)_2(C_5H_5)_2][L]$. The reaction mechanism is discussed. A complex mechanism can be shown to be quantitatively consistent with the data for the reaction with tri-*n*-butylphosphine.

## Introduction

While reactions of tetracarbonylnickel(0) with monodentate ligands have been extensively studied,[1-4] there are few reports of such reactions with di-μ-carbonyl-bis(cyclopentadienyl)dinickel(0). King has shown that tris(dimethylamino)phosphine (tdp) reacts with $Ni_2(CO)_2(C_5H_5)_2$ to give $Ni(CO)_2(tdp)_2$ and nickelocene[5] (eq 1, L = tdp), while a recent report[6] describes the reaction of $Ni_2(CO)_2(C_5H_5)_2$ with bis(diphenylphosphino)acetylene to give $Ni_2(CO)_2[(C_6H_5)_2PC_2P(C_6H_5)_2]_3$. Interestingly, both reactions involve the displacement of a cyclopentadienyl moiety from nickel. It has been found (*vide infra*) that monodentate ligands (phos-

$$Ni_2(CO)_2(C_5H_5)_2 + 2L \longrightarrow Ni(CO)_2L_2 + Ni(C_5H_5)_2 \qquad (1)$$

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(1) L. S. Meriwether and M. L. Fiene, *J. Amer. Chem. Soc.*, **81**, 4200 (1959).

(2) J. P. Day, F. Basolo, R. G. Pearson, L. F. Kangas, and P. M. Henry, *ibid.*, **90**, 1925 (1968).

(3) J. P. Day, F. Basolo, and R. G. Pearson, *ibid.*, **90**, 6927 (1968).

(4) J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1378 (1960).

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

(6) A. J. Carty, A. Efraty, and T. W. Ng, *Can. J. Chem.*, **47**, 1429 (1969).

phines, phosphites, arsines, and CO) quite generally react with $Ni(CO)_2(C_5H_5)_2$ according to (1). While complications have been encountered with some ligands, most of these reactions proceed smoothly to completion at room temperature.

The most common reaction of metal carbonyl complexes with phosphines and other Lewis bases is the displacement of carbon monoxide. Among the reactions of organo transition metal complexes, such reactions have been the most extensively studied from a mechanistic standpoint.[7] In contrast the kinetics of few reactions have been studied where the cyclopentadienyl ligand is involved as either an entering or leaving group. An exception is a recently reported[8] kinetic study of the displacement of both cyclopentadienyl ligands from nickelocene by triethyl phosphite to give tetrakis(triethyl phosphite)nickel(0). This reaction is first order in nickelocene and second order in phosphite, strongly implying the intermediacy of a nickelocene–phosphite adduct. The fate of the cyclopentadienyl groups is unclear.

In this light, reaction 1 is of particular interest; the cyclopentadienyl ligand serves as a leaving group with respect to one nickel and an entering group with respect to the other. A kinetic study was undertaken in the hope of gaining an appreciation of this mechanism which would shed some light on both roles.

## Experimental Section

All operations involving air-sensitive materials were carried out under an atmosphere of argon or prepurified nitrogen.

**Materials.**—Di-$\mu$-dicarbonyl-bis(cyclopentadienyl)dinickel(0) was prepared and recrystallized from diethyl ether as described in the literature;[9,10] mp 139–141.5°, lit.[9] mp 139°. *Anal.* Calcd for $C_{12}H_{10}Ni_2O_2$: C, 47.47; H, 3.32. Found: C, 47.50; H, 3.38. Bis(triphenylphosphine)- and bis(triphenyl phosphite)-dicarbonylnickel(0) were prepared by treating the appropriate ligand with tetracarbonylnickel(0) in toluene. The desired products crystallized from the reaction solutions and, after washing with hexane, required no further purification.

All other materials were obtained commercially. Solvents were dried and deoxygenated by distillation from calcium hydride in an atmosphere of nitrogen. Tri-*n*-butylphosphine was distilled in an atmosphere of nitrogen at reduced pressure. Nickelocene was dissolved in toluene at room temperature and recrystallized at −78°. Triphenylarsine was dissolved in boiling ethanol and recrystallized at room temperature. Other reagents were used as received.

**Kinetic Runs.**—A weighed portion of one reagent (usually the nickel complex) was introduced into a nitrogen-filled Schlenk tube and dissolved in a known volume of deoxygenated solvent delivered by pipet. This solution was then placed in a controlled-temperature bath (±0.1°) at least 20 min prior to beginning the run. Reactions were initiated by adding the other reagent either as the weighed solid, in a small volume of stock solution (tri-*n*-butylphosphine, ethyldiphenylphosphine), or as the pure liquid (triphenyl phosphite). The course of the reaction was monitored by removal of aliquots with a syringe through a stainless steel needle and examination of their spectra in a 1.0-mm KBr cell over the region 2100–1800 $cm^{-1}$. The reaction mixture was protected during removal of aliquots by a countercurrent of argon. For slower runs where the time required to record the spectrum was negligible on the time scale of the reaction, the only time recorded was that at which the ir scan was initiated. For experiments in which the reaction time was comparatively short, a record was made of the exact time at which each peak was measured.

That exposure to ambient laboratory lighting has no effect on the observed kinetics was verified in experiments with triphenylphosphine. Reaction mixtures kept in foil-wrapped vessels displayed behavior identical with that of unprotected solutions.

Reaction with carbon monoxide according to (1) was studied in toluene by following the uptake of carbon monoxide. A thermostated gas buret was joined to a thermostated reaction vessel *via* a short length of capillary tubing. The entire system was flushed thoroughly with nitrogen, and a known volume of $Ni_2(CO)_2(C_5H_5)_2$ solution, previously prepared to known concentration, was introduced. Reaction was initiated by flushing the system with carbon monoxide, bubbled through the substrate solution, for 20 min. Negligible reaction occurred in this time. The system was then adjusted to a convenient volume and sealed at atmospheric pressure. The solution was continuously stirred as vigorously as possible with a magnetic bar, and the decrease in gas volume was monitored as a function of time. The total volume changes observed in these experiments were in excellent agreement with those required by quantitative reaction according to (1). The concentration of dissolved carbon monoxide in these solutions was estimated from tabulated data;[11] corrections to atmospheric pressure and appropriate temperatures were made by assuming the validity of Henry's law and making use of an approximate treatment described by Hildebrand.[12]

As noted by Fischer and Palm,[9] $Ni_2(CO)_2(C_5H_5)_2$ decomposes slowly in solution. Control experiments established that this decomposition was too slow (<5% in 48 hr) to compete significantly with the reactions of interest.

Except as discussed below, rate constants were evaluated graphically in the usual manner.

**Infrared Measurements.**—All spectra for kinetic runs were taken on a Perkin-Elmer 621 with a matched cell containing pure solvent in the reference beam. With cells filled with pure solvent, the ordinate was calibrated at infinite and zero absorbance before each run. At a given frequency Beer's law is obeyed by absorbances calculated from peak heights. For a given instrument setting, the precision of this approach is quite good. The day to day reproducibility is somewhat less satisfactory. Variations of up to ±5% were noted in extinction coefficients calculated for the same complex from measurements made on solutions prepared at different times. Band positions were obtained from spectra calibrated *vs.* a polystyrene reference.

**Spectrometric Characterization of Reaction Products.**—For the ligands triphenylphosphine, triphenyl phosphite, and ethyldiphenylphosphine, all available evidence indicates that reaction with $Ni_2(CO)_2(C_5H_5)_2$ takes place cleanly and quantitatively according to (1). With these ligands the infinite-time carbonyl region spectra of reaction mixtures agree within experimental error in both band positions and band intensities with expectations based on spectra of authentic $Ni(CO)_2L_2$ solutions of known concentrations. Table I presents the band positions observed in this work. In the cases of the triphenylphosphine and triphenyl phosphite complexes, comparison solutions were prepared by weight using the pure solids.

Bis(ethyldiphenylphosphine)dicarbonylnickel(0) was prepared *in situ* for this comparison. A stock solution of tetracarbonylnickel(0) was prepared by weight. A portion of this solution and an excess of ethyldiphenylphosphine were diluted

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[7] (a) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, Chapter 7; (b) R. J. Angelici, *Organometal. Chem. Rev.*, **3**, 173 (1968).

[8] H. Werner, V. Harder, and E. Deckelmann, *Helv. Chim. Acta*, **52**, 1081 (1969).

[9] E. O. Fischer and C. Palm, *Chem. Ber.*, **91**, 1725 (1958).

[10] J. F. Tilney-Bassett, *J. Chem. Soc.*, 577 (1961).

[11] W. F. Linke, "Solubilities," Vol. I, 4th ed, Van Nostrand, Princeton, N. J., 1958, p 457.

[12] J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," 3rd ed, American Chemical Society Monograph Series, No. 17, Reinhold, New York, N. Y., 1950, p 241.

TABLE I
CO STRETCHING FREQUENCIES FOR
$Ni(CO)_2L_2$ COMPLEXES ($cm^{-1}$)

| L | Obsd, this work | Lit. |
|---|---|---|
| $P(C_6H_5)_3$ | 2014, 1954 | 2000, 1955[a] |
| $P(OC_6H_5)_3$ | 2040, 1999 | 2040, 1995[a] |
| $P(n\text{-}C_4H_9)_3$ | 1995, 1935 | 1995, 1930[a] |
| $P(C_2H_5)(C_6H_5)_2$ | 2002, 1948 | 2000, 1940[b] |
| $As(C_6H_5)_3$ | 2007, 1940 | 2072, 1995, 1941 (*sic*)[c] |

[a] Reference 1. [b] L. S. Meriwether, M. F. Leto, E. C. Colthup, and G. W. Kennerly, *J. Org. Chem.*, **27**, 3930 (1962). [c] Reference 4.

to a tetracarbonylnickel(0) concentration comparable to substrate concentrations in the kinetic runs. After 48 hr reaction was complete giving a spectrum in agreement with that previously reported for bis(ethyldiphenylphosphine)dicarbonylnickel(0) (Table I).

Carbonyl region ir spectra of reaction mixtures containing $Ni_2(CO)_2(C_5H_5)_2$ and tri-*n*-butylphosphine depend in a complex way on both time and initial reagent concentrations (*vide infra*). However, when this reaction is carried out with a significant excess of tri-*n*-butylphosphine, the "infinite-time" spectrum corresponds to that reported for $Ni(CO)_2[P(n\text{-}C_4H_9)_3]_2$. Moreover, the band intensities under these circumstances are in quantitative agreement with those expected by comparison with authentic $Ni(CO)_2[P(n\text{-}C_4H_9)_3]_2$ assuming quantitative reaction according to (1). The authentic complex was prepared *in situ* from tetracarbonylnickel(0) and excess tri-*n*-butylphosphine in the manner described above for the corresponding ethyldiphenylphosphine complex.

**Isolation of Products from Reaction with $P(C_6H_5)_3$.**—To substantiate further the stoichiometry indicated by (1) and unequivocally establish that nickelocene is a product, the reaction with triphenylphosphine was carried out on a preparative scale. Thus, 0.561 g (1.85 mmol) of $Ni_2(CO)_2(C_5H_5)_2$ and 0.985 g (3.76 mmol) of $P(C_6H_5)_3$ were covered with 60 ml of cyclohexane and the mixture was vigorously stirred. After 6 hr the solution became dark green and a substantial quantity of colorless, crystalline precipitate was present. The solid was recovered by filtration, washed with additional cyclohexane, and dried under vacuum to give 1.03 g of $Ni(CO)_2[P(C_6H_5)_3]_2$ (87% yield based on (1)) whose identity was confirmed by comparison of its infrared spectrum to that of authentic material (KBr pellets). The green filtrate was concentrated to dryness and the residue was taken up in a minimum of toluene at room temperature. The toluene solution was filtered and cooled slowly to −78° depositing large green needles. These were recovered, washed with cyclohexane, and dried under vacuum to give 0.233 g of $Ni(C_5H_5)_2$ (67% yield based on (1)) whose identity was also confirmed by comparison of its infrared spectrum to that of authentic material (KBr pellets).

**Isolation of $Ni(C_5H_5)_2$ from Reaction with $P(n\text{-}C_4H_9)_3$.**—In view of the complications observed with tri-*n*-butylphosphine, it was deemed necessary to demonstrate that nickelocene is also produced in this case. Accordingly, 0.607 g (2.00 mmol) of $Ni_2(CO)_2(C_5H_5)_2$ was treated in 25 ml of toluene with 0.884 g (4.36 mmol) of $P(n\text{-}C_4H_9)_3$. After 7 hr the solution was concentrated to 5 ml and chromatographed on deoxygenated silica gel. The chromatogram was developed with toluene, and a green band, which was followed by a red one, was eluted first. The green eluate was collected and concentrated to approximately 4 ml from which 0.105 g of nickelocene (28% yield based on (1)) was recovered and identified as described above. The modest recovery of nickelocene in this experiment is attributed primarily to losses incurred during work-up; nickelocene does not chromatograph well.

**Isolation of Products from Reaction with $As(C_6H_5)_3$.**—Attempts to prepare bis(triphenylarsine)dicarbonylnickel(0) from tetracarbonylnickel(0) and excess triphenylarsine were unsuccessful. The instability of bis(triphenylarsine)dicarbonylnickel(0) in solution has been noted previously.[4] However, the available evidence indicates that bis(triphenylarsine)dicarbonylnickel(0) is produced when triphenylarsine reacts with $Ni_2(CO)_2(C_5H_5)_2$. When the ir spectra of these reaction solutions are monitored with time, bands appear at 2007 and 1940 $cm^{-1}$ as the substrate bands decay. To extents increasing with increasing time and increasing temperature, the intensities of these bands subsequently begin to decrease and new bands at *ca.* 2060 and 2003 $cm^{-1}$ appear in the spectra.

The bands at 2007 and 1940 $cm^{-1}$ are assigned to bis(triphenylarsine)dicarbonylnickel(0). This is based on isolation of products from a preparative-scale reaction. Thus 0.602 g (1.98 mmol) of $Ni_2(CO)_2(C_5H_5)_2$ and 1.22 g (3.98 mmol) of $As(C_6H_5)_3$ were allowed to react in 15 ml of cyclohexane with continuous stirring. After 24 hr the solution had become brown-green and extensive precipitation of a colorless powder had occurred. The powder was recovered by filtration, washed with additional cyclohexane, and dried under vacuum to give 0.757 g (53% yield based on (1)) of $Ni(CO)_2[As(C_6H_5)_3]_2$, whose composition was confirmed by elemental analysis. *Anal.* Calcd for $C_{38}H_{30}As_2NiO_2$: C, 62.8; H, 4.16; As, 20.6; Ni, 8.07. Found: C, 62.1; H, 4.17; As, 18.5; Ni, 7.31. The ir spectrum of this material agrees well with that of the initial product in the kinetic runs. The filtrate was concentrated to dryness and the residue was taken up in a minimum of toluene. Crystallization and identification of nickelocene (0.253 g, 68% yield based on (1)) was effected as described above.

## Results

The reactions of di-$\mu$-carbonyl-bis(cyclopentadienyl)-dinickel(0) with triphenylphosphine, ethyldiphenylphosphine, and triphenyl phosphite in decalin were characterized by perfectly straightforward kinetic behavior. Spectra of these reaction mixtures displayed only the characteristic absorbances of the reactant and the products. In all three cases the kinetics were strictly second order, first order in the ligand and first order in $Ni_2(CO)_2(C_5H_5)_2$. Moreover, rate constants were calculated from the decay of the $Ni_2(CO)_2(C_5H_5)_2$ absorption at 1855 $cm^{-1}$ as well as from the growth of the two $Ni(CO)_2L_2$ absorption bands. In all cases, the rate constants calculated for decay of substrate and for appearance of product were in good agreement.

In most cases these reactions were run with an excess of the ligand present. However, reactions in which triphenylphosphine was present at less than the stoichiometrically required concentration ($[P(C_6H_5)_3]_0 < 2[Ni_2(CO)_2(C_5H_5)_2]_0$) still gave results corresponding to quantitative reaction according to (1). Rate constants calculated in these cases were in agreement with those obtained when triphenylphosphine was present in excess. As discussed in detail below, this is in marked contrast to the behavior observed when tri-*n*-butylphosphine is the ligand.

The reaction with triphenylphosphine was also studied in THF. Using 1-mm ir cells, only the substrate band was unobscured by solvent absorptions. The reaction was again first order in each reagent. In view of the modest effect on the rate, solvent effects were not studied further.

As noted above, study of the reaction with triphenylarsine was complicated by further reaction of the initial product, $Ni(CO)_2[As(C_6H_5)_3]_2$. For this reason and due to the fact that absorptions in the terminal CO region due to triphenylarsine were quite large for the high concentrations used in several runs, the rate constant was evaluated solely from the rate at which the substrate band decayed. The ultimate fate of the $Ni(CO)_2[As(C_6H_5)_3]_2$ produced is not clear. The ir bands produced upon further reaction of this material do however correspond to those observed when tetracarbonylnickel(0) is treated with triphenylarsine under similar conditions. A possibility is that some decomposition occurs with liberation of carbon monoxide, which then reacts with additional $Ni(CO)_2[As(C_6H_5)_3]_2$ to give $Ni(CO)_3As(C_6H_5)_3$. In any event these kinetic studies were carried out with at least a tenfold excess of triphenylarsine so that the release or consumption of $As(C_6H_5)_3$ by the following reaction would have negligible effect on the observed rate of substrate consumption.

The rapid exchange of $^{14}CO$ with the carbonyl groups of $Ni(CO)_2(C_5H_5)_2$ in toluene solution has been previously investigated.[13] The rate of carbon monoxide exchange was found to be first order in both $Ni_2(CO)_2(C_5H_5)_2$ and carbon monoxide. In the present work it has been found that bubbling carbon monoxide through a decalin solution of $Ni_2(CO)_2(C_5H_5)_2$ results in a slow decay of the absorption due to starting material and the concomitant appearance of a band at 2057 cm$^{-1}$, attributed to tetracarbonylnickel(0). In agreement with this assignment, it is observed that an increase in the rate of carbon monoxide bubbling can lead to a decrease in the height of this new peak as tetracarbonylnickel(0) is swept from the solution. No effort has been made to determine an accurate rate constant for this reaction in decalin. However, in an experiment at 22° with an ambient pressure (*ca.* 730 Torr) of carbon monoxide above a CO-saturated solution, the absorption due to $Ni_2(CO)_2(C_5H_5)_2$ decayed with a first-order rate constant of approximately $4.5 \times 10^{-6}$ sec$^{-1}$. Taking the concentration of dissolved carbon monoxide[14] as $1.2 \times 10^{-2}$ $M$ gives a second-order rate constant of approximately $4 \times 10^{-4}$ $M^{-1}$ sec$^{-1}$.

A more accurate rate constant was determined for this reaction in toluene to permit a direct comparison with the carbon monoxide exchange results. In this case the reaction was observed by following carbon monoxide consumption. Since the carbon monoxide concentration could not be readily varied in the available apparatus, the order in carbon monoxide, presumed to be one by comparison to the other ligands, was not verified. At 30° the rate of reaction 1 with carbon monoxide is slower by a factor of 70 than the rate of carbon monoxide exchange,[15] $k_{ex} = 1.1 \times 10^{-1}$ $M^{-1}$ sec$^{-1}$. Hence very little reaction according to (1) would occur in the time required for essentially complete exchange.

Rate constants and activation parameters obtained for these ligands are summarized in Tables II and III.

TABLE II[g]

RATE CONSTANTS OBSERVED FOR

$$Ni_2(CO)_2(C_5H_5)_2 + 2L \longrightarrow Ni(CO)_2L_2 + Ni(C_5H_5)_2$$

| Ligand | $10^3[L]$, $M$ | $10^3[Ni_2(CO)_2(C_5H_5)_2]$, $M$ | Temp, °C | Solvent[h] | $10^3k$, $M^{-1}$ sec$^{-1}$ |
|---|---|---|---|---|---|
| CO | 7.0 | 4.17 | 30 | T | 1.6[f] |
| CO | 6.48 | 3.82 | 40 | T | 4.82[f] |
| CO | 6.04 | 4.03 | 50 | T | 10.2[f] |
| CO | 12.0 | 1.80 | 22 | D | 0.4[f] |
| $P(OC_6H_5)_3$ | 71.8 | 1.80 | 30 | D | 12.4 |
| $P(OC_6H_5)_3$ | 35.7 | 1.52 | 30 | D | 13.0 |
| $P(OC_6H_5)_3$ | 17.2 | 1.43 | 30 | D | 11.3 |
| $P(OC_6H_5)_3$ | 7.50 | 1.99 | 30 | D | 12.9[a] |
| $P(OC_6H_5)_3$ | 37.2 | 1.40 | 40 | D | 29.4 |
| $P(OC_6H_5)_3$ | 18.6 | 1.26 | 40 | D | 31.9 |
| $P(OC_6H_5)_3$ | 18.6 | 1.18 | 50 | D | 72.2 |
| $P(OC_6H_5)_3$ | 18.6 | 1.17 | 50 | D | 71.0 |
| $P(C_6H_5)_3$ | 19.2 | 1.98 | 30 | D | 31.5 |
| $P(C_6H_5)_3$ | 30.3 | 15.1 | 30 | D | 31.2[a,b] |
| $P(C_6H_5)_3$ | 35.9 | 1.12 | 30 | D | 30.6 |
| $P(C_6H_5)_3$ | 3.25 | 1.97 | 30 | D | 31.0[a] |
| $P(C_6H_5)_3$ | 21.4 | 0.74 | 30 | D | 30.4 |
| $P(C_6H_5)_3$ | 10.4 | 0.74 | 30 | D | 34.6 |
| $P(C_6H_5)_3$ | 2.37 | 7.53 | 30 | D | 31.0[a,c] |
| $P(C_6H_5)_3$ | 25.4 | 0.98 | 30 | D | 30.0[d] |
| $P(C_6H_5)_3$ | 3.61 | 1.78 | 40 | D | 77.5[a] |
| $P(C_6H_5)_3$ | 8.65 | 1.78 | 40 | D | 76.5[a] |
| $P(C_6H_5)_3$ | 3.96 | 1.28 | 50 | D | 151[a] |
| $P(C_6H_5)_3$ | 4.98 | 1.06 | 50 | D | 154[a] |
| $P(C_6H_5)_3$ | 14.5 | 1.07 | 30 | F | 16.1[e] |
| $P(C_6H_5)_3$ | 29.6 | 2.08 | 30 | F | 17.0[e] |
| $P(C_6H_5)_3$ | 45.9 | 2.24 | 30 | F | 16.9[e] |
| $As(C_6H_5)_3$ | 29.8 | 1.56 | 30 | D | 3.44[e] |
| $As(C_6H_5)_3$ | 67.2 | 1.07 | 30 | D | 3.49[e] |
| $As(C_6H_5)_3$ | 146 | 1.09 | 30 | D | 3.50[e] |
| $As(C_6H_5)_3$ | 28.6 | 1.60 | 40 | D | 8.52[e] |
| $As(C_6H_5)_3$ | 135 | 1.65 | 40 | D | 8.52[e] |
| $As(C_6H_5)_3$ | 16.1 | 1.50 | 50 | D | 21.2[e] |
| $As(C_6H_5)_3$ | 32.9 | 1.48 | 50 | D | 20.6[e] |
| $P(C_2H_5)(C_6H_5)_2$ | 3.72 | 1.28 | 30 | D | 62.3 |
| $P(C_2H_5)(C_6H_5)_2$ | 17.2 | 1.15 | 30 | D | 58.0 |
| $P(C_2H_5)(C_6H_5)_2$ | 7.29 | 1.53 | 30 | D | 61.4 |

[a] Calcd from second-order integrated equation. [b] A 0.1-mm ir cell. [c] Calcd from product bands only. [d] Light excluded. [e] Calcd from substrate band only. [f] By gas absorption. [g] Rate constants are as defined by $-d[Ni_2(CO)_2(C_5H_5)_2]/dt = -(d[L]/dt)/2 = k[Ni_2(CO)_2(C_5H_5)_2][L]$. Except as otherwise noted, rate constants are average values calculated from appearance of two product bands and disappearance of one reactant band. [h] Abbreviations: T, toluene; D, decalin; F, tetrahydrofuran.

TABLE III

RATE CONSTANTS AND ACTIVATION PARAMETERS FOR

$$Ni_2(CO)_2(C_5H_5)_2 + 2L \longrightarrow Ni(CO)_2L_2 + Ni(C_5H_5)_2$$

| Ligand | Solvent[a] | $10^3k$, $M^{-1}$ sec$^{-1}$ | | | $\Delta H^{\ddagger}$, kcal/mol | $\Delta S^{\ddagger}$, cal/deg mol |
|---|---|---|---|---|---|---|
| | | 30° | 40° | 50° | | |
| CO | T | 1.6 | 4.8 | 10.2 | 17.4 ± 2 | ... |
| $As(C_6H_5)_3$ | D | 3.5 | 8.5 | 21 | 17.1 ± 1 | −14 ± 3 |
| $P(OC_6H_5)_3$ | D | 12.5 | 31 | 72 | 16.4 ± 1 | −13 ± 3 |
| $P(C_6H_5)_3$ | F | 16.7 | ... | ... | ... | ... |
| $P(C_6H_5)_3$ | D | 31 | 77 | 153 | 14.9 ± 1 | −16 ± 3 |
| $P(C_2H_5)(C_6H_5)_2$ | D | 61 | ... | ... | ..... | ... |
| $P(n\text{-}C_4H_9)_3$ | D | 400[b] | ... | ... | ... | ... |

[a] Abbreviations: T, toluene; D, decalin; F, tetrahydrofuran. [b] See text.

The reaction of $Ni_2(CO)_2(C_5H_5)_2$ with tri-*n*-butylphosphine shows several interesting features. The rate of the reaction is dependent on the concentrations of both reagents, but the rate is sufficiently great that it was necessary to study the reaction under circumstances where the reagent concentrations were comparable. As mentioned above, when this reaction is carried out with a significant excess ($\geq 5 \times 10^{-4}$ $M$) of tri-

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[13] A. Wojcicki and F. Basolo, *J. Inorg. Nucl. Chem.*, **17**, 77 (1961).

[14] The value given for heptane[11] was used.

[15] Estimated from the 25 and 0° data of ref 13.

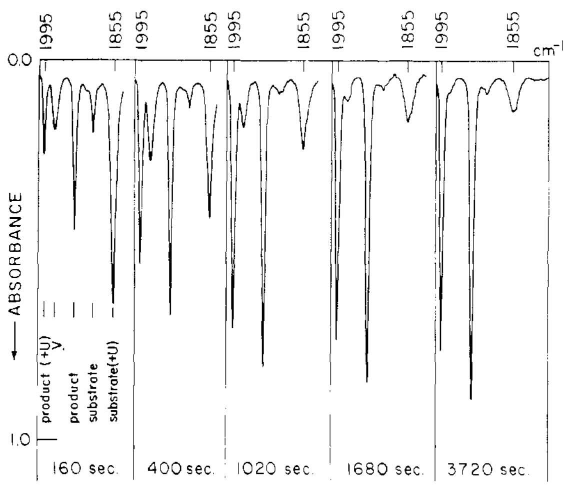

Figure 1.—Spectra of reaction mixture as a function of time. $[\mathrm{Ni_2(CO)_2(C_5H_5)_2}]_0$ = 1.41 m*M*; $[\mathrm{P}(n\text{-}\mathrm{C_4H_9})_3]_0$ = 4.27 m*M*.

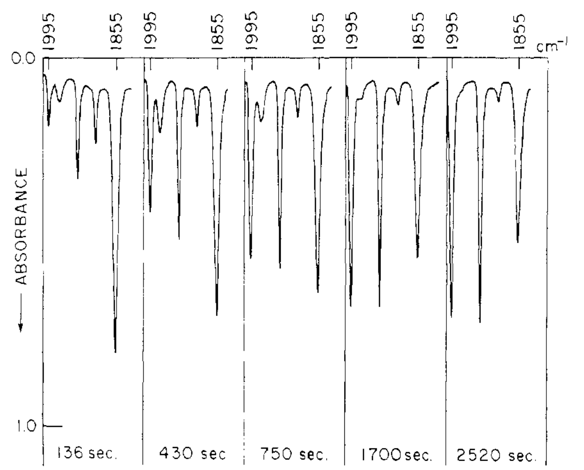

Figure 2.—Spectra of reaction mixture as a function of time. $[\mathrm{Ni_2(CO)_2C_5H_5)_2}]_0$ = 1.59 m*M*; $[\mathrm{P}(n\text{-}\mathrm{C_4H_9})_3]_0$ = 1.95 m*M*.

*n*-butylphosphine, the infinite-time spectrum is that of $\mathrm{Ni(CO)_2[P(}n\text{-}\mathrm{C_4H_9)_3]_2}$. However, even under these circumstances, plots of the kinetic data appropriate for a second-order rate law do not exhibit satisfactory linearity.

In view of the known reactions of some phosphines and phosphites with nickelocene at higher temperatures,[8,16] the possibility arises that the anomalies in this reaction are due in part to further reaction between nickelocene produced *via* (1) and additional tri-*n*-butylphosphine. Two lines of evidence establish that no such reaction occurs under the conditions of the kinetic studies. First, several kinetic runs were carried out in which a large excess of nickelocene was present initially ($[\mathrm{Ni(C_5H_5)_2}]_0 > 10[\mathrm{P}(n\text{-}\mathrm{C_4H_9})_3]_0$). Experiments differing only by the absence of added nickelocene gave essentially identical results. These experiments also effectively exclude the possibility that reaction according to (1) does not go to completion for thermodynamic reasons when L is tri-*n*-butylphosphine. Second, a series of solutions was prepared in which nickelocene and tri-*n*-butylphosphine were present at concentrations approximating those in the kinetic runs. When oxygen is carefully excluded from these solutions, their visible spectra are those of nickelocene for times long compared to the time required for consumption of $\mathrm{Ni_2(CO)_2(C_5H_5)_2}$ in the rate studies.

It has been possible to collect good absorbance *vs.* time data in experiments where the initial tri-*n*-butylphosphine to substrate concentration ratio varies from 0.52 to 4.3. While this is not a particularly wide concentration range, the variation in behavior observed within this range is remarkable.

In all runs, the band at 1855 cm$^{-1}$, due to $\mathrm{Ni_2(CO)_2(C_5H_5)_2}$, decreases in intensity while new bands appear at 1995 and 1935 cm$^{-1}$, the appropriate positions for $\mathrm{Ni(CO)_2[P(}n\text{-}\mathrm{C_4H_9)_3]_2}$. However, the intensity ratio for these latter two peaks is not constant. (See Figures 1 and 2.) It must be concluded that an additional species, which absorbs at either or both of these frequencies, is present. For convenience, this species will be referred to as "U." Now, the absorbance ratio [absorbance at 1995 cm$^{-1}$/absorbance at 1935 cm$^{-1}$] appropriate for $\mathrm{Ni(CO)_2[P(}n\text{-}\mathrm{C_4H_9)_3]_2}$ is 0.64. At reaction times short enough that the band at 1855 cm$^{-1}$ is still present, the absorbance ratio for these two bands is invariably greater than 0.64. While U could absorb at both 1995 and 1935 cm$^{-1}$, the simplest possibility is that it absorbs only at 1995 cm$^{-1}$.

In addition, a relatively weak peak is observed to grow at 1974 cm$^{-1}$, reach a maximum absorbance after 5–12 min, and then decay away. This peak clearly does not arise from either the reactants or the products. Moreover, it cannot arise from the species U responsible for the anomalous behavior of the product peaks. This is established by the fact that when the reaction is carried out with an excess of $\mathrm{Ni_2(CO)_2(C_5H_5)_2}$ the ratio of the absorbance at 1995 cm$^{-1}$ to that at 1935 cm$^{-1}$ is significantly greater than 0.64 at times long enough so that the band at 1974 cm$^{-1}$ has vanished completely (Figure 2). Therefore, it is necessary to conclude that the band at 1974 cm$^{-1}$ arises from a third, terminal CO-containing species, which will be referred to as "V."

Further anomalies are associated with the time dependence of the absorbance at 1855 cm$^{-1}$. In experiments run with an excess of ligand ($[\mathrm{P}(n\text{-}\mathrm{C_4H_9})_3]_0 > 2[\mathrm{Ni_2(CO)_2(C_5H_5)_2}]_0$), this band decays rapidly to a small residual absorption. This residual absorption then decays to zero only very slowly. The conclusion that a species containing at least one bridging CO group is produced in these solutions seems inescapable. There are two alternative possibilites. The first is that the rate law for consumption of $\mathrm{Ni_2(CO)_2(C_5H_5)_2}$ involves a higher power of the tri-*n*-butylphosphine concentration. This possibility has been excluded on the basis that the falloff in the rate of decay of the 1855-cm$^{-1}$ band is too extreme to be accounted for by any reasonable order in tri-*n*-butylphosphine concentration. The second alternative is that reaction 1 has a small equilibrium constant where L = $\mathrm{P}(n\text{-}\mathrm{C_4H_9})_3$. As noted above this possibility is excluded by the fact that addition of excess nickelocene to reaction mixtures has a negligible effect

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[16] J. R. Olechowski, C. G. McAlister, and R. F. Clark, *Inorg. Chem.*, **4**, 246 (1965).

on the course of this reaction. The simplest interpretation consistent with these observations is that U absorbs at 1855 $cm^{-1}$ as well as at 1995 $cm^{-1}$.

On the other hand, in experiments with an excess of metal carbonyl ($[P(n\text{-}C_4H_9)_3]_0 < 2[Ni_2(CO)_2(C_5H_5)_2]_0$), the 1855-$cm^{-1}$ band decays to give a significantly *lower* absorbance at long times than is calculated assuming the stoichiometry of (1); hence, on the average, less than 2 mol of tri-*n*-butylphosphine is consumed per mole of $Ni_2(CO)_2(C_5H_5)_2$. Assuming that the only carbonyl-containing species present are $Ni(CO)_2[P(n\text{-}C_4H_9)_3]_2$ and U, it can be concluded that production of U consumes less than 2 mol of tri-*n*-butylphosphine per mole of $Ni_2(CO)_2(C_5H_5)_2$.

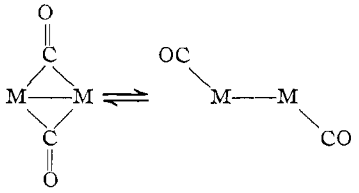
In summary, the minimal assumptions necessary for interpretation of the observations on the reaction of tri-*n*-butylphosphine with $Ni_2(CO)_2(C_5H_5)_2$ require the presence of species of U and V. U has absorption bands at 1995 and 1855 $cm^{-1}$, while V has a band at 1974 $cm^{-1}$. In the presence of excess tri-*n*-butylphosphine, both U and V are converted to $Ni(CO)_2[P(n\text{-}C_4H_9)_3]_2$, but in the absence of sufficient tri-*n*-butylphosphine, U persists in these solutions for a considerable period.

## Discussion

It is useful to observe that the reverse of reaction 1 occurs when L is carbon monoxide; indeed this is the route by which $Ni_2(CO)_2(C_5H_5)_2$ is prepared.[9] It is reasonable to suppose that the reverse reaction is mechanistically analogous to other substitution reactions of diliganddicarbonylnickel(0) complexes in which case the initial step involves dissociation of ligand to give liganddicarbonylnickel(0).[1-3] Therefore by microscopic reversibility it must be anticipated that the reactions studied here lead to diliganddicarbonylnickel(0) *via* the same three-coordinate species.

Cleavage to monomeric $Ni(CO)(C_5H_5)$ radicals has been postulated[17] to explain the products observed in the high-temperature decompostion of $Ni_2(CO)_2(C_5H_5)_2$. Since monomeric $Co(CO)_4$ radicals are produced on vacuum pyrolysis of the formally isoelectronic octacarbonyldicobalt(0),[18] it might be anticipated that the nickel radicals would be similarly accessible. Apparently this is not the case; when $Ni_2(CO)_2(C_5H_5)$ is subjected to treatment similar to that yielding $Co(CO)_4$ radicals, no epr evidence for the presence of $Ni(CO)(C_5H_5)$ in the sublimate could be observed.[19] Since, moreover, it is difficult to imagine a mechanism involving this radical which is both plausible and consistent with the experimental evidence, it will not be considered further as a possible intermediate in the mechanism of (1).

Also, by analogy to octacarbonyldicobalt(0),[20] it is possible that a nonbridged isomer of $Ni_2(CO)_2(C_5H_5)_2$ exists in equilibrium with the bridged form in solution. There is no direct evidence for this equilibrium, but such isomerism has been demonstrated for the analogous compound bis(cyclopentadienyl)di(cyclohexyl isocyanide)dinickel(0).[21] It has recently been proposed that interconversions of structures with bridged and nonbridged carbonyl groups are facile processes.[22] If this is the case, the experiments described here could not be expected to detect the intervention of a nonbridged isomer of $Ni_2(CO)_2(C_5H_5)_2$ in the mechanism of (1).



Direct evidence for the presence of intermediates in these reactions has been obtained only in the case of tri-*n*-butylphosphine. Even in this case it is probably necessary to postulate a pathway with no detectable intermediates (*vide infra*) in order to account adequately for the experimental data. On this basis the simplest possible mechanism for (1) is a single-step process initiated by direct attack of the ligand at a nickel atom. This is consistent with the second-order rate law and with the negative entropies of activation, which are similar in magnitude to those observed for bimolecular displacements of CO by π-acceptor ligands from other other metal carbonyl substrates.[7b] Moreover, the order of ligand reactivity typically observed[7b] in such cases is the same as is found for (1).

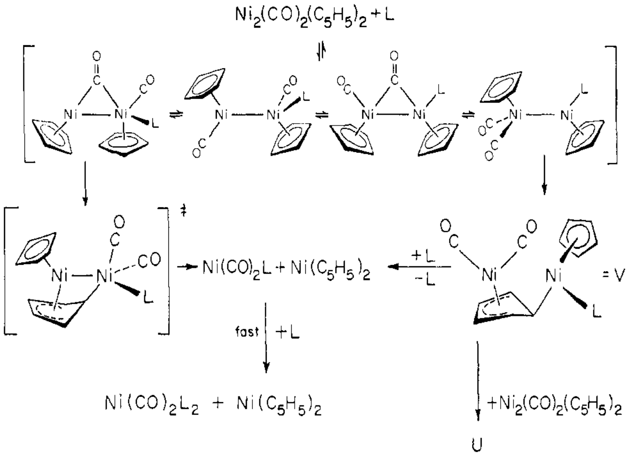


Figure 3.—Summary of the mechanistic possibilities discussed.

Examination of molecular models suggests a facile course for such a mechanism. If the attack by the incoming ligand asymmetrically cleaves the CO bridges such that both CO groups become bound to the same nickel as the incoming ligand, the reaction complex can rotate about the nickel–nickel bond in such a way as to bring the migrating cyclopentadienyl ring within bonding distance of the other nickel atom. This would lead to a transition-state structure similar to that shown in Figure 3. Similar transition-state structures have been

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(17) G. G. Petukhov, V. I. Ermolaev, and R. V. Kaplina, *Zh. Obshch. Khim.*, **38**, 465 (1968).

(18) H. J. Keller and H. Wawersik, *Z. Naturforsch.*, **20**, 938 (1965).

(19) A. H. Maki and R. Allendoerfer, private communication.

(20) K. Noack, *Spectrochim. Acta*, **19**, 1925 (1963); *Helv. Chim. Acta*, **47**, 1064 (1964).

(21) Y. Yamamoto and N. Hagihara, *Bull. Chem. Soc. Jap.*, **39**, 1084 (1966).

(22) J. G. Bullitt, F. A. Cotton, and T. J. Marks, *J. Amer. Chem. Soc.*, **92**, 2155 (1970).

postulated previously to rationalize the products obtained in other reactions where a cyclopentadienyl group is transferred intermolecularly to or from a nickel atom.[23]

Now, if it is desired to modify this mechanism so as to account for the exchange as well as the substitution behavior of carbon monoxide by a single pathway, it is necessary to introduce an intermediate species whose formation scrambles incoming with bound carbon monoxide and which can return to starting material as well as go on to products. The bracketed structures represented in Figure 3 could be taken as possible formulations for this intermediate.

The fact that the species labeled "U" is formed as a relatively stable product in the reaction with tri-*n*-butylphosphine constitutes an unfortunate complication. Since the composition of this species is unknown while a complete mechanism must take its presence into account, any mechanism suggested will rest upon a more or less arbitrary assumption as to the composition of U. On the other hand, V is clearly an intermediate in this system. It is of considerable interest whether V is an intermediate in the production of $\mathrm{Ni(CO)_2[P(\textit{n}\text{-}C_4H_9)_3]_2}$ or merely an intermediate in a side reaction leading to U. For this reason a vigorous effort was made to find a mechanism which would quantitatively account for the absorbance *vs.* time data collected.

The approach taken was to utilize a computerized numerical integration scheme to test the compatibility of plausible mechanisms with the observed kinetic data. This involved assuming a reaction mechanism, including compositions for U and V. If these assumptions are correct and the true rate constants as well as the extinction coefficients for U and V are known, numerical integration would give calculated absorbance *vs.* time data in agreement with that actually observed.[24] Since neither the rate constants nor the extinction coefficients are known, a least-squares-based, iterative refinement procedure was programmed. Starting from a guessed set of values for the rate constants and unknown extinction coefficients, the program adjusts the values of these parameters to optimize agreement between calculated and observed absorbance *vs.* time data. The test of a given mechanism is, of course, whether there exists a set of rate constants and extinction coefficients which yield, by numerical integration, calculated absorbance *vs.* time data within experimental error of the experimentally observed values. This refinement procedure is similar to a slightly more mathematically sophisticated program previously described.[25]

More possible mechanisms for this reaction have been examined than can be discussed here. However, it has not been possible to find a satisfactory mechanism by which V was the *only* route to $\mathrm{Ni(CO)_2[P(\textit{n}\text{-}C_4H_9)_3]_2}$. One reason for this failure lies in the fact that V was present to a maximal extent at least 5 min after initiation of the reaction. However, appearance of product began immediately; no induction period has been observed for either of the product bands. If reaction exclusively *via* V is satisfactorily to reproduce the time dependence of the 1995- and 1935-$\mathrm{cm^{-1}}$ bands, it appears inevitable that the time of maximal absorbance at 1974 $\mathrm{cm^{-1}}$ must be less than half of what is actually observed.

In contrast, if it is supposed that an effectively single-step process as envisioned above occurs, a relatively simple mechanism gives a good quantitative fit to the observed kinetic data. This mechanism, (2)–(6), entails parallel paths to the product $\mathrm{Ni(CO)_2[P(\textit{n}\text{-}C_4H_9)_3]_2}$, one direct and one through the intermediate V. In this interpretation U is assigned the composition $\mathrm{Ni_3(CO)_4(C_5H_5)_2P(\textit{n}\text{-}C_4H_9)_3}$ (or, possibly, $\mathrm{Ni_4(CO)_4(C_5H_5)_4P(\textit{n}\text{-}C_4H_9)_3}$). Figures 4 and 5 compare calculated absorbance *vs.* time data to the experimental results for the runs whose spectra are displayed in Figures 1 and 2, respectively. Optimum rate constants for steps 2–5 are, respectively, 0.40, 0.40, 0.48, and 2.08 $M^{-1}\ \mathrm{sec^{-1}}$. The optimum extinction coefficients for U are 4670 and 5760 $M^{-1}\ \mathrm{cm^{-1}}$ at 1995 and 1855 $\mathrm{cm^{-1}}$, respectively, while that of V at 1974 $\mathrm{cm^{-1}}$ is 3840 $M^{-1}\ \mathrm{cm^{-1}}$. In

$$\mathrm{Ni(CO)_2(C_5H_5)_2 + P(\textit{n}\text{-}C_4H_9)_3 \longrightarrow Ni(CO)_2P(\textit{n}\text{-}C_4H_9)_3 + Ni(C_5H_5)_2} \qquad (2)$$

$$\mathrm{Ni_2(CO)_2(C_5H_5)_2 + P(\textit{n}\text{-}C_4H_9)_3 \longrightarrow V} \qquad (3)$$

$$\mathrm{V + P(\textit{n}\text{-}C_4H_9)_3 \longrightarrow Ni(CO)_2P(\textit{n}\text{-}C_4H_9)_3 + Ni(C_5H_5)_2 + P(\textit{n}\text{-}C_4H_9)_3} \qquad (4)$$

$$\mathrm{V + Ni_2(CO)_2(C_5H_5)_2 \longrightarrow U + Ni(C_5H_5)_2} \qquad (5)$$

$$\mathrm{Ni(CO)_2P(\textit{n}\text{-}C_4H_9)_3 + P(\textit{n}\text{-}C_4H_9)_3 \xrightarrow{\text{fast}} Ni(CO)_2[P(\textit{n}\text{-}C_4H_9)_3]_2} \qquad (6)$$

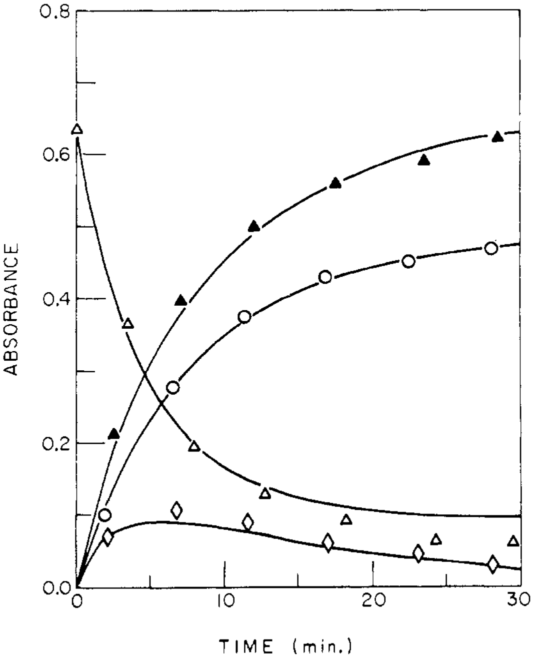

Figure 4.—Absorbance *vs.* time data for the experiment of Figure 1. Solid lines are calculated from the mechanism, rate constants, and extinction coefficients given in the text. Points are experimental: open triangles, 1855 $\mathrm{cm^{-1}}$; filled triangles, 1935 $\mathrm{cm^{-1}}$; circles, 1995 $\mathrm{cm^{-1}}$; diamonds, 1974 $\mathrm{cm^{-1}}$.

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(23) P. M. Maitlis, A. Efraty, and M. L. Games, *J. Am. Chem. Soc.*, **87**, 719 (1965).

(24) D. F. DeTar, *J. Chem. Educ.*, **44**, 191 (1967).

(25) W. E. Ball and L. C. D. Groenweghe, *Ind. Eng. Chem., Fundam.*, **5**, 181 (1966).

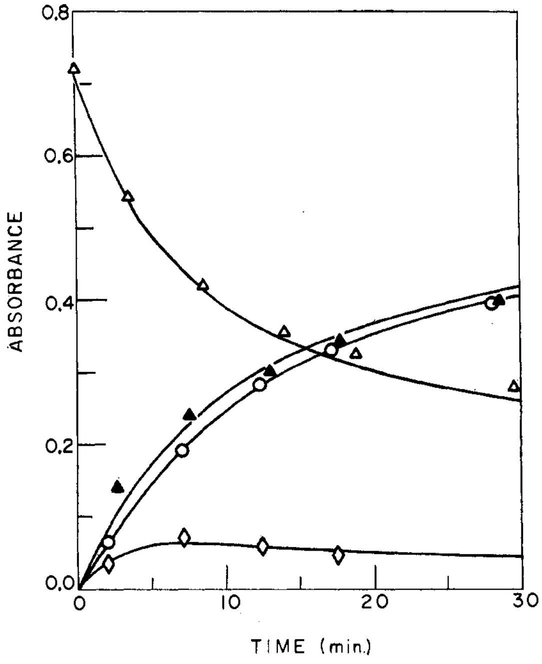

Figure 5.—Absorbance *vs.* time data for the experiment of Figure 2. The conventions of Figure 4 apply.

comparison the extinction coefficient of $Ni_2(CO)_2(C_5H_5)_2$ at 1855 $cm^{-1}$ is 4500 $M^{-1}$ $cm^{-1}$ while those of $Ni(CO)_2[P(n-C_4H_9)_3]_2$ are 3950 and 6200 $M^{-1}$ $cm^{-1}$ at 1995 and 1935, respectively.

The essential consequence of the fit of this mechanism to the experimental data is that such a dual role for V is compatible with the available evidence while mechanisms in which V is the only route to $Ni(CO)_2[P(n-C_4H_9)_3]_2$ are not. The question then becomes: Is there a comparably simple mechanism compatible with the experimental data by which V does not lead to $Ni(CO)_2[P(n-C_4H_9)_3]_2$? Unfortunately, even within the framework of tentative conclusions erected above to explain the observations on this system, an answer to this question has not been forthcoming; it has not been possible to fit the experimental data to a mechanism of this type. However, even if such a mechanism were found, the anomalies observed with tri-*n*-butylphosphine would not necessarily be irrelevant to the mechanism of (1) since the U formed in the presence of excess tri-*n*-butylphosphine eventually disappears to form bis(tri-*n*-butylphosphine)dicarbonyldinickel and (presumably) nickelocene.

In summary, the mechanism of (2)–(6) is the simplest which is demonstrably compatible with the experimental data. This mechanism can accommodate the rapid exchange of carbon monoxide either by the intervention of an unobserved intermediate in step 2, as suggested above, or by rapid equilibration with a species analogous to V. The results with the other ligands are also readily accommodated so long as the rate constant for step 4 is much larger than those for steps 3 and 5. Of course, with this proviso, either (2) or (3) could be negligibly slow.

Figure 3 describes the mechanistic conclusions arrived at above in terms of some possible structures for the various species. A variety of structures can be considered for an adduct of the composition $Ni_2(CO)_2(C_5H_5)_2L$. If it is generally true that interconversion of bridged and nonbridged isomers is rapid,[22] any or all of the structures in brackets could plausibly describe undetected intermediates in the mechanism of (1). However, it is important to remember that, so long as an analog of V is accessible with carbon monoxide to accommodate the rapid carbon monoxide exchange, no other intermediate is *necessary* to explain the kinetic data. The structure depicted for V has the advantage that its reactions according to (4) and (5) are readily rationalized. Since it could be considered to arise through a transition-state structure similar to the symmetrical (when L is carbon monoxide), bridged structure shown, this structure for V is capable of rationalizing the exchange of carbon monoxide. On the other hand, any of the other structures would represent more intuitively plausible species for explaining this exchange.

Finally, it must be noted that the role and structure assigned to V in Figure 3 represent a structural rationalization of the fact that (2)–(6) gives a reasonably good fit to the experimental results when L is tri-*n*-butylphosphine. It is possible that another mechanism could be found which would give an adequate fit to the absorbance *vs.* time data and which would permit assignment of one of the bracketed structures to V.

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