allowed to warm slowly (2 hr) to room temperature while 200 ml of gas (12.4% ethylene) was collected by water displacement. The ethylene fraction of the gas product was purified by glc and analyzed for deuterium content by high-resolution mass spectrometry. Only a trace of deuterated ethylene was noted (0.16% C_2H_3D); the product was essentially free of higher-deuterated ethylenes.

The solid product was then filtered, washed with anhydrous ether, air-dried, and pyrolyzed at 320°. The methane fraction of the gas product was analyzed by mass spectrometry: 11% CD_4, 19% CHD_3, 41% CH_2D_2, 10% CH_3D, 19% CH_4.

Decomposition of the Methylene-Containing Complex in Chloroform. The methylene-containing complex (0.14 g) was dissolved in 2 ml of chloroform with warming. After approximately 3 min, a gray precipitate formed which was filtered and dried over phosphorus pentoxide. The infrared spectrum of the dried product (15 mg) exhibited only minor bands which could be attributed to I or to the methylene-containing complex and showed strong methylene bands at 2924 and 2850 cm^{-1} and polymethylene bands at 730 and 719 cm^{-1}. *Anal.* Found: C, 46.7; H, 8.4; H:C (atomic), 2.16. The thin layer chromatogram of the chloroform-soluble product showed a yellow spot of high intensity which corresponded in position and hue to that of I.

Reaction of the Methylene-Containing Complex with Cyclohexene. The methylene-containing complex (0.15 g) was added to cyclohexene (4.2 g) and the mixture refluxed with stirring for 6 hr. Glc of the crude product showed only a trace of a compound corresponding to norcarane. The reaction was repeated in a sealed tube at 200° for 20 min. Again, only a trace (*ca.* 0.3%) of norcarane was noted in the liquid product.

Reaction of the Methylene-Containing Complex with Styrene. A mixture of the methylene-containing complex (0.86 g) and styrene (1.29 g) was warmed on a steam bath for 20 min. The resulting dark mixture, upon treatment with pentane, yielded a yellow precipitate and turned amber in color. The infrared spectrum of the yellow solid was essentially that of I with minor bands corresponding to unchanged methylene-containing complex. The

quantity of I (approximated by tlc and infrared) found in the crude solid product seemed to be sensitive to reaction conditions and reagent quality. The products varied between being nearly all I and containing only detectable quantities in addition to decomposition products. In all cases, however, the solid product appeared richer in I than did the starting methylene-containing complex. The filtrate contained two products which were isolated by glc and analyzed by mass spectrometry. Both compounds were C_9H_{10} hydrocarbons and gave fragmentation patterns consistent with those found for genuine samples of phenylcyclopropane and α-methylstyrene. In addition, the two products proved identical with phenylcyclopropane and α-methylstyrene by glc (peak enhancement with genuine samples) on three different columns (SF-96, Bentone, and Ucon Polar). Yields (based on the iridium complex) were as high as 22% for phenylcyclopropane and 9% for α-methylstyrene.

Phenylcyclopropane. The procedure used for the preparation of phenylcyclopropane was essentially that reported by Doering and Roth.[9] Diazomethane (prepared from 4.5 g of Du Pont EXR-101)[28] was distilled from ether solution into a stirred mixture of 25 ml of ether, 0.5 g of cuprous chloride, and 1.5 g of styrene at 0°. After 1 hr of stirring, the product was filtered and the ether solvent distilled from the filtrate. The product contained two components (glc), the larger having the composition C_9H_{10} (mass spectrometry), $n^{20}D$ 1.5322; lit[30] $n^{20}D$ 1.5325. The infrared spectrum (film) contained all the characteristic bands reported[30] for phenylcyclopropane.

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Kinetics and Mechanism of Substitution Reactions of π-Cyclopentadienyldicarbonylrhodium

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Abstract: This paper reports the synthesis and properties of some mono- and disubstituted derivatives of C_5H_5-Rh(CO)$_2$ containing phosphines, phosphites, and isonitriles. The rate of replacement of carbon monoxide is first order in both the substrate and the reagent concentrations. Phosphine, phosphites, and isonitriles are good reagents, whereas under similar conditions pyridine and triphenylarsine do not react. The results are in agreement with the substrate being a class b or soft metal.

Several kinetic studies have been made of the exchange of carbon monoxide and of substitution reactions with metal carbonyls and their derivatives. Most of the systems investigated react at rates that do not depend on the entering ligand, and the results obtained provide information on the properties that affect the reactivities of different substrates. For example, Meriwether and Fiene[2] observed that the rate of replacement of phosphine from Ni(CO)$_2$(PR$_3$)$_2$ decreases with increasing base strength of the phosphine. Likewise, the rate of replacement of carbon monoxide from

$Mn(CO)_5Cl$ is greater than it is from $Mn(CO)_5I$,[3] and the rate of carbon monoxide exchange[4a] with $Mo(CO)_6$, and of its substitution reactions,[4b] is faster than it is for the corresponding chromium and tungsten hexacarbonyls. Heck[5] finds that the reaction of RCOCo(CO)$_4$ with triphenylphosphine is subject to steric acceleration.

Although quantitative kinetic data are available on substrate reactivities in these systems, no systematic

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study has been reported on reagent reactivities toward a given substrate. One reason for this is that many of the reactions proceed by a dissociation process which does not depend on the reagent. However, some of these reactions are known to involve a bimolecular displacement mechanism, and such reactions can be used to investigate the nucleophilic strengths of various reagents. For example, the rates of exchange of carbon monoxide with $C_5H_5Co(CO)_2$ and with $(C_5H_5)_2$-$Ni_2(CO)_2$ are first order in substrate and first order in carbon monoxide concentrations.[6] Similarly, the rate of reaction of $CoNO(CO)_3$ with triphenylphosphine is second order, and it is about twice as fast as the rate of the analogous reaction with $P(OCH_2)_3CCH_3$.[7] Recent studies have been made of the reactivity of various reagents toward $CoNO(CO)_3$ and $Fe(NO)_2(CO)_2$.[8]

This paper reports kinetic data on the replacement of carbon monoxide from $C_5H_5Rh(CO)_2$ with different reagents. The syntheses and characterizations of some of the substitution products are described. Mention is also made of limited observations on reactions of the analogous cobalt and iridium compounds.

Experimental Section

Compounds and Solvents. The compounds $C_5H_5Co(CO)_2$,[9] $C_5H_5Rh(CO)_2$,[10] and $C_5H_5Ir(CO)_2$[11] were prepared by the methods described in the literature. The compounds were purified by repeated distillation under high vacuum in the dark.

The reagents $P(C_6H_5)_3$, $As(C_6H_5)_3$, $P(OC_6H_5)_3$, and pyridine were Eastman Organic Chemicals, White Label products, and were used without further purification. n-Butyl phosphite and $P(OCH_3)_3$ were also obtained from Eastman Organic Chemicals, but these were distilled before use. The phosphines[12] $P(n\text{-}C_4H_9)_3$, $P(C_2H_5)_3$, $P(C_2H_5)_2C_6H_5$, $P(p\text{-}CH_3OC_6H_4)_3$, and $P(C_6H_{11})_3$, as well as the isonitriles[13] $p\text{-}CH_3C_6H_4NC$ and $C_6H_{11}NC$, were prepared by the methods described in the literature. We wish to thank Dr. J. G. Verkade, Iowa State University, for the gift of $P(OCH_2)_3CCH_3$ which was purified by extraction into ether and sublimation of the residue after evaporation of the ether.

The solvents toluene, hexane, and tetrahydrofuran were distilled from sodium under nitrogen and stored under nitrogen. Nitromethane, Spectrograde from Eastman Organic Chemicals, was saturated with nitrogen before use.

Preparation of Substitution Products. All operations in the syntheses of these compounds were carried out under an atmosphere of nitrogen.

π-**Cyclopentadienylcarbonyl(triphenylphosphine)cobalt.** A reaction mixture containing 276 mg of $C_5H_5Co(CO)_2$ (1.53 mmoles) and 402 mg of $P(C_6H_5)_3$ (1.53 mmoles) in 40 ml of hexane was refluxed for 40 hr. Upon cooling the solution to room temperature, red-brown crystals separated. These were collected on a filter and then twice recrystallized from benzene-hexane in a ratio of 1:4. The product, dried at room temperature under high vacuum, weighed 470 mg (75% yield) and had a melting point of 142°, in agreement with that for the compound prepared independently.[14]

Anal. Calcd for $C_5H_5CoCOP(C_6H_5)_3$: C, 69.57; H, 4.87; Co, 14.23. Found: C, 69.18; H, 5.15; Co, 14.34.

Meaningful values of molecular weight could not be obtained because the compound decomposes too fast in oxygen-containing solutions.

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The infrared spectrum in Nujol mull showed 3102 vw, 2940–2850 ss (Nujol), 2722 w, 2670 vw, 1938–1921 s, 1610 vw, 1589 w, 1573 vw, 1463–1378 s (Nujol), 1356 w, 1311 w, 1266 w, 1182 w, 1162 vw, 1152 vw, 1107 w, 1086 m, 1078 w, 1044 w, 1023 w, 1009 w, 993 m, 976 vw, 928 vw, 916 vw, 906 vw, 895 vw, 860 w, 842 w, 831 w, 805 m, 756 s, 745 vs, 722 m, 693 vs, 686 s, 620 w, 597 s, 559 s, 534 s, 514 sh, 508 s, 483 w, 447 m, and 435 w cm^{-1}.

π-**Cyclopentadienylcarbonyl(triphenylphosphine)rhodium.** A reaction mixture containing 250 mg of $C_5H_5Rh(CO)_2$ (1.1 moles) and 280 mg of $P(C_6H_5)_3$ (1.07 moles) in 40 ml of hexane was refluxed for 12 hr. After the removal of about 10 ml of solvent and cooling to room temperature, red crystals separated from solution. These were collected on a suction filter, washed with hexane, and dried at room temperature under vacuum. The product weighed 400 mg (80% yield) and had mp 153°.

Anal. Calcd for $C_5H_5RhCOP(C_6H_5)_3$: C, 62.90; H, 4.39; mol wt, 458. Found: C, 63.31; H, 4.70; mol wt, 454.

The infrared spectrum in Nujol mull showed 3190 vw, 3076 vw, 2940–2850 vs (Nujol), 2670 vw, 1942 vs, 1589 w, 1573 vw, 1463–1378 s (Nujol), 1356 w, 1311 w, 1266 vw, 1186 w, 1164 w, 1156 vw, 1106 vw, 1092 s, 1072 w, 1045 w, 1028 w, 1011 w, 998 w, 978 w, 920 vw, 903 vw, 894 vw, 858 w, 846 w, 831 w, 790 s, 758 m, 747 s, 724 w, 707 m, 695 vs, 689 sh, 619 vw, 563 s, 534 s, 521 s, 511 s, 504 s, 468 m, and 441 m cm^{-1}.

π-**Cyclopentadienylcarbonyl(tri-n-butylphosphine)rhodium.** A reaction mixture containing 224 mg of $C_5H_5Rh(CO)_2$ (1.0 mmole) and 0.26 ml of $P(n\text{-}C_4H_9)_3$ (1 mmole) in 40 ml of hexane was refluxed for 2 hr. The solution was then filtered and about 20 ml of solvent was removed under vacuum. This solution was cooled to −80°, and the yellow crystals that separated were collected on a suction filter at −80°. The product, dried under vacuum at 0°, weighed 210 mg (53% yield) and had mp 34°. The compound is very soluble in organic solvents.

Anal. Calcd for $C_5H_5RhCOP(C_4H_9)_3$: C, 54.27; H, 8.10; mol wt, 398. Found: C, 53.94; H, 7.97; mol wt, 392.

The infrared spectrum in Nujol mull showed 3108 vw, 3088 vw, 2940–2850 vs (Nujol), 1940 vs, 1463–1378 s (Nujol), 1302 w, 1208 w, 1107 vw, 1093 w, 1050 w, 1012 w, 986 w, 970 w, 909 m, 773 s, 724 m, 559 m, and 521 w cm^{-1}.

π-**Cyclopentadienylcarbonyl(4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane)rhodium.** A reaction mixture containing 293 mg of $C_5H_5Rh(CO)_2$ (1.3 mmoles) and 190 mg of $P(OCH_2)_3CCH_3$ (1.28 mmoles) in 50 ml of hexane was allowed to stand at 40° for 50 hr. During this time yellow crystals separated from solution and these were collected on a suction filter. The infrared spectrum of the filtrate was examined in the carbonyl region, and it showed only the presence of unreacted $C_5H_5Rh(CO)_2$. The nmr spectrum of the crystalline product indicated that it was a mixture of C_5H_5-$RhCOP(OCH_2)_3CCH_3$ and $C_5H_5Rh(P(OCH_2)_3CCH_3)_2$ in the approximate ratio of 3:2. The mixture was separated by sublimation under high vacuum at 120°. The monosubstituted derivative which sublimed was collected and recrystallized from a 1:1 mixture of benzene and hexane. The product, dried under vacuum at room temperature, weighed 153 mg (34% yield) and did not melt but sublimed at 120°.

Anal. Calcd for $C_5H_5RhCOP(OCH_2)_3CCH_3$: C, 38.39; H, 4.10; mol wt, 344. Found: C, 37.88; H, 4.77; mol wt, 351.

The infrared spectrum in Nujol mull showed 3110 w, 2940–2850 vs (Nujol), 2724 w, 1963 vs, 1914 w, 1463 s (Nujol), 1400 m, 1378 s (Nujol), 1350 m, 1304 w, 1186 w, 1170 s, 1119 v, 1104 w, 1031 vs, 1015 vs, 979 m, 951 s, 928 s, 868 s, 776 vs, broad, 724 sh, 658 vs, 553 s, 535 w, 517 s, and 472 m cm^{-1}.

π-**Cyclopentadienyl{bis(4-methyl-2,6,7-trioxa-1-phosphabicyclo-[2.2.2]octane)}rhodium.** The residue that remained, after the sublimation described above, was recrystallized from a 1:1 mixture of benzene and hexane. The yellow needles obtained were dried under vacuum at room temperature and weighed 166 mg (28% yield). The compound decomposes at 215°.

Anal. Calcd for $C_5H_5Rh(P(OCH_2)_3CCH_3)_2$: C, 38.81; H, 4.99; mol wt, 464. Found: C, 38.66; H, 5.08; mol wt, 459.

The infrared spectrum in Nujol mull showed 3109 vw, 3075 vw, 2940–2850 vs (Nujol), 2713 vw, 1463–1378 s (Nujol), 1348 w, 1303 vw, 1171 m, 1054 m, 1041 m, 1031 s, 1016 vs, 973 w, 959 w, 931 m, 868 s, 800 s, 755 vs, 748 vs, 677 s, 666 s, 656 s, 527 m, and 498 vw cm^{-1}.

π-**Cyclopentadienylcarbonyl(trimethyl phosphite)rhodium.** A reaction mixture containing 286 mg of $C_5H_5Rh(CO)_2$ (1.28 mmoles) and 0.15 ml of $P(OCH_3)_3$ (1.2 mmoles) in 25 ml of hexane was allowed to stand at 40° for 40 hr. Removal of the solvent under vacuum resulted in the formation of a red oil. The oil was placed

on an alumina column (Merck reagent grade aluminium oxide) and eluted with hexane. This gave a solution of $C_5H_5Rh(CO)_2$ and permitted the removal of unreacted starting material. Elution of the column with 1:1 hexane–benzene gave a solution of C_5H_5-RhCOP(OCH$_3$)$_3$. The solvent was removed at reduced pressures, and the dark green oil obtained resisted all attempts to cause it to crystallize.

Anal. Calcd for $C_5H_5RhCOP(OCH_3)_3$: C, 33.66; H, 4.71. Found: C, 34.22; H, 4.39.

The infrared spectrum of the liquid showed 3111 w, 3082 w, 2972 m, 2940 m, 2891 w, 2838 m, 1969 vs, 1800 w, 1740 w, 1465 sh, 1443 m, 1408 w, 1368 w, 1350 vw, 1242 w, 1180 m, 1107 vw, 1060 sh, 1020 vs, 783 vs, 756 vs, 681 w, 555 m, 511 m, and 485 w cm^{-1}.

π-Cyclopentadienyl[bis(trimethyl phosphite)]rhodium. The subsequent elution of the column described above with diethyl ether gave a red solution. The solvent was removed under vacuum and a dark red oil was obtained, which could not be caused to crystallize.

Anal. Calcd for $C_5H_5Rh(P(OCH_3)_3)_2$: C, 31.75; H, 5.75. Found: C, 31.42; H, 5.72.

The infrared spectrum of the liquid showed 3100 w, 2975 w, 2941 m, 2892 w, 2834 m, 1774 vw, 1464 m, 1440 w, 1409 vw, 1339 vw, 1290 vw, 1182 m, 1030 vs, broad, 835 w, 805 s, broad, 771 vs, broad, 724 vs, and 539 s.

π-Cyclopentadienylcarbonyl(cyclohexylisonitrile)rhodium. A reaction mixture containing 278 mg of $C_5H_5Rh(CO)_2$ (1.25 mmoles) and 0.15 ml of $C_6H_{11}NC$ (1.3 mmoles) in 20 ml of hexane was allowed to stand for 1 hr at 40°. After filtering through a thin layer of alumina and removing the solvent to leave about 5 ml of solution, it was cooled to −80° and yellow crystals separated. The crystals were collected on a suction filter at −80° and dried under vacuum at −10°. The product weighed 232 mg (61% yield) and had mp 34°.

Anal. Calcd for $C_5H_5RhCOCNC_6H_{11}$: C, 51.16; H, 5.28; N, 4.59; mol wt, 305. Found: C, 51.34; H, 5.27; N, 4.79; mol wt, 300.

The infrared spectrum of the molten compound between KBr plates showed 3198 w, 3092 m, 2932 vs, 2845 s, 2133 vs, 1952 vs, 1449 m, 1400 w, 1362 s, 1349 m, 1324 m, 1315 sh, 1270 vw, 1262 vw, 1151 w, 1113 w, 1107 vw, 1046 w, 1014 m, 984 w, 930 w, 893 w, 863 w, 783 vs, 661 w, 582 m, 563 m, 512 m, 502 m, and 437 m cm^{-1}.

Reactions of Substituted Compounds with Carbon Monoxide. Some qualitative observations have been made on the reversibility of the reactions in these systems. Solutions of the substituted compounds were saturated with CO at atmospheric pressure and any changes in the infrared spectra of the solutions with time were observed.

Carbon monoxide was bubbled through a 0.007 M solution of $C_5H_5RhCOP(C_6H_5)_3$ in toluene for a period of 16 hr at room temperature. During this time there was no evidence for the formation of $C_5H_5Rh(CO)_2$.

Similar treatment of a 0.008 M solution of $C_5H_5Rh(P(OCH_2)_3$-CCH$_3$)$_2$ resulted in the appearance of a strong absorption band at 1979 cm^{-1} due to the formation of $C_5H_5RhCOP(OCH_2)_3CCH_3$. Further treatment with CO increased this band only slightly, but after 48 hr a band appeared at 2050 cm^{-1} due to the formation of $C_5H_5Rh(CO)_2$. This same behavior was observed when CO was also bubbled through a solution of $C_5H_5Rh(P(n-OC_4H_9)_3)_2$.

Kinetic Studies. The rates of the substitution reactions were followed by observing changes in the infrared spectra of the reaction mixtures and also by measuring the rate of CO evolution. All of the kinetic studies were carried out under pseudo-first-order conditions, using at least a tenfold excess of reagent. Light and air were always excluded. No detectable change in the infrared spectrum of a 0.01 M toluene solution of $C_5H_5Rh(CO)_2$ occurred during 1 week in the dark at 40°. Tetrahydrofuran and nitromethane solutions of the compound showed about a 10% decrease in the intensity of the carbonyl absorption after storing for 3 days at 40° in the dark. The rate constants obtained by the infrared and the CO evolution methods were in good agreement and were reproducible to within 10% or better. The probable errors in the values are estimated to be ±1 kcal/mole for ΔH^* and ±2 eu for ΔS^*.

The infrared data were obtained with a Perkin-Elmer Model 337 spectrophotometer equipped with an external recorder. The rates of reaction were determined by following the disappearance of the highest-frequency, carbonyl-stretching absorption of the substrate. The reaction mixtures were kept in a constant temperature bath, and small samples were removed at various times to determine the infrared spectra. Usually about 20 measurements were made

during a period of 3 half-lives. Since an excess of reagent was used, all reactions proceeded to completion. Good linear plots were obtained from the data by plotting log (log I_0/I) *vs.* t, where I is the transmittance at time t, and I_0 is the transmittance of the base line.

The CO evolution data were obtained using the gasometric apparatus described earlier.[15] Either 15 or 25 ml of the reagent solution was equilibrated with CO at atmospheric pressure in a thermostated reaction vessel. Then a concentrated solution of $C_5H_5Rh(CO)_2$ was injected into the vessel with a hypodermic syringe. Particular attention was payed to vigorous stirring of the reaction mixture by means of a magnetic stirrer in order to avoid supersaturation of the solution with the CO evolved. The volume of gas liberated was measured at atmospheric pressure with a mercury gas buret and about 20 readings were made during the period of 3 half-lives for the reaction. Good linear plots of the data were obtained for the reactions with phosphines by plotting log ($V - V_\infty$) *vs.* t, where V is the volume at time t, and V_∞ is the volume at infinite time. For phosphine reagents, the experimental infinite-time volume was always in good agreement with the calculated volume corresponding to the release of 1 mole of CO per mole of $C_5H_5Rh(CO)_2$. For the reaction with $P(n-OC_4H_9)_3$, the amount of CO released corresponded to 1.6 moles per mole of substrate, and the infrared spectrum showed the presence of small amounts of starting material as well as the mono- and the disubstituted derivatives. Therefore, rate constants were not obtained from these data. The isonitrile reagents react with $C_5H_5Rh(CO)_2$ to give V_∞ corresponding to the release of both molecules of CO.

The method used to investigate the rate of ^{14}CO exchange with $C_5H_5Rh(CO)_2$ was similar to that described earlier,[16] the chief modification being the apparatus used to measure the radioactivity of the gas phase. This was done with a 100-ml DCF ion chamber and the electrometer system "Dynacon" Model 6010 obtained from Nuclear Chicago. The experimental infinite-time activities were in good agreement with the calculated values based on the exchange of both of the CO molecules in the compound. However, the rates of exchange were not reproducible. Freshly prepared solutions of the complex exchanged much slower than did aged solutions. Likewise, the rate of exchange appeared to increase with an increase in the radioactivity of the system. That exchange of ^{14}CO with $C_5H_5Rh(CO)_2$ does occur at 0° was reported by Cramer.[17]

Results

Some of the mono- and disubstituted derivatives of $C_5H_5Rh(CO)_2$ were prepared and characterized by means of analyses (performed by Micro-Tech, Skokie, Ill.) and molecular weights. The infrared spectrum in the carbonyl region of a given derivative was in good agreement with that of the reaction mixture at infinite time containing the same reagent as did the derivative. Reaction mixtures for which the product was not isolated gave infrared spectra analogous to either the mono- or disubstituted derivatives.

The pseudo-first-order rate constants for the reaction of $C_5H_5M(CO)_2$ with $P(C_6H_5)_3$, where M = Co, Rh, and Ir, are given in Table I.

Table I. Pseudo-First-Order Rate Constants for the Reaction $C_5H_5M(CO)_2 + P(C_6H_5)_3 \rightarrow$ $C_5H_5MCOP(C_6H_5)_3 + CO$ in Toluene at 40°

	[C_5H_5M- $(CO)_2$], M	[$P(C_6H_5)_3$], M	10^6k, sec^{-1}	ν_{CO}, cm^{-1} [a]
$C_5H_5Co(CO)_2$	0.00193	0.147	4.5	2037, 1965
$C_5H_5Rh(CO)_2$	0.00132	0.147	46	2051, 1987
$C_5H_5Ir(CO)_2$	0.00201	0.147	2.1	2037, 1957

[a] The C–O stretching frequencies of the $C_5H_5M(CO)_2$ compound, ref 11.

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Table II. Rate Constants for the Reaction $C_5H_5Rh(CO)_2 + L \rightarrow$ $C_5H_5RhCOL + CO$ in Toluene at 40° with Changes in Concentration of L

L	$[C_5H_5Rh-(CO)_2]$, M	[L], M	$10^5 k_{obsd}$, sec^{-1}	$10^4 k$, M^{-1} sec^{-1}
$P(n\text{-}C_4H_9)_3$	0.004	0.053	17.5	33
$P(n\text{-}C_4H_9)_3$	0.008	0.122	38.3	32[a]
$P(n\text{-}C_4H_9)_3$	0.012	0.188	66	35
$P(n\text{-}C_4H_9)_3$	0.002	0.245	86	34
$P(n\text{-}C_4H_9)_3$	0.008	0.410	130	32[a]
$P(n\text{-}OC_4H_9)_3$	0.0024	0.088	3.55	4.0
$P(n\text{-}OC_4H_9)_3$	0.0013	0.147	5.6	3.8
$P(n\text{-}OC_4H_9)_3$	0.0024	0.234	8.0	3.4
$P(n\text{-}OC_4H_9)_3$	0.0012	0.660	25.3	3.8

[a] The reaction was followed by the rate of CO evolution. Other data were obtained by the infrared method.

Table III. Rate Constants for the Reaction $C_5H_5Rh(CO)_2 +$ $L \rightarrow C_5H_5RhCOL + CO$ in Toluene at 40° with Changes in the Nature of L

L	k, M^{-1} sec^{-1}	ΔHNP[a]
$P(OC_6H_5)_3$	7.3×10^{-5}	875
$P(C_6H_{11})_3$	7.7×10^{-5}	33
$P(C_6H_5)_3$	2.9×10^{-4}	573
$P(OC_4H_9)_3$	3.8×10^{-4}	520[b]
$P(n\text{-}OC_4H_9)_3$	5.6×10^{-4}	...
$P(p\text{-}CH_3OC_6H_4)_3$	5.6×10^{-4}	493
$P(C_4H_9)_3$	3.3×10^{-3}	131
$P(n\text{-}C_4H_9)_3$	4.3×10^{-3}	300
$P(C_2H_5)_3$	8.0×10^{-3}	111
C_5H_5N	Very slow[c]	286
$As(C_6H_5)_3$	Very slow[c]	...

[a] Difference in half-neutralization potential between L and N,N'-diphenylguanidine in nitromethane. The smaller ΔHNP, the more basic is L.[18] [b] Value for $P(OC_2H_5)_3$. [c] No detectable reaction after 3 days with 0.1 M reagent.

Table IV. Activation Parameters and Solvent Effects for the Reaction $C_5H_5Rh(CO)_2 + L \rightarrow C_5H_5RhCOL + CO$

Solvent	L	Temp, °C	$10^3 k$, M^{-1} sec^{-1}	ΔH^*, kcal/mole	ΔS^*, eu
Toluene	$P(C_2H_5)_2C_6H_5$	40	4.3	15	-20
Toluene	$P(C_2H_5)_2C_6H_5$	25	1.2		
Toluene	$P(n\text{-}OC_4H_9)_3$	40	0.38	18	-16
Toluene	$P(n\text{-}OC_4H_9)_3$	25	0.084		
THF[a]	$P(C_2H_5)_2C_6H_5$	40	2.45	13	-28
THF[a]	$P(C_2H_5)_2C_6H_5$	25	0.79		
THF[a]	$P(n\text{-}OC_4H_9)_3$	40	0.22	16	-23
THF[a]	$P(n\text{-}OC_4H_9)_3$	25	0.055		
CH_3NO_2	$P(C_2H_5)_2C_6H_5$	40	3.7	13	-27
CH_3NO_2	$P(C_2H_5)_2C_6H_5$	25	1.2		
CH_3NO_2	$P(n\text{-}OC_4H_9)_3$	40	0.27	15	-26
CH_3NO_2	$P(n\text{-}OC_4H_9)_3$	25	0.076		

[a]Tetrahydrofuran.

The dependence of the rate of reaction 1 on the concentration of reagent L is shown by the data in Table II for L = $P(n\text{-}C_4H_9)_3$ and $P(n\text{-}OC_4H_9)_3$. Table III

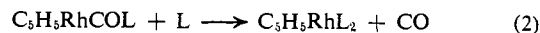$$C_5H_5Rh(CO)_2 + L \longrightarrow C_5H_5RhCOL + CO \qquad (1)$$

contains kinetic data for the reaction of this substrate with various reagents and also gives the relative basicities of some of the reagents.[18] Under these experimental conditions, there was no reaction of the car-

(18) C. A. Streuli, *Anal. Chem.*, **32**, 985 (1960), and private communication.

bonyl with either pyridine or triphenylarsine. Data on the activation parameters in three different solvents are given in Table IV.

Both CO molecules are replaced from $C_5H_5Rh(CO)_2$ by phosphites and isonitriles. Rate data for reaction 2

$$C_5H_5RhCOL + L \longrightarrow C_5H_5RhL_2 + CO \qquad (2)$$

are recorded in Table V.

Table V. Rate Constants for the Reaction $C_5H_5RhCOL + L \rightarrow$ $C_5H_5RhL_2 + CO$ in Toluene at 40°

L	$[C_5H_5Rh-(CO)_2]$, M	[L], M	$10^6 \times k_{obsd}$, sec^{-1}	k, M^{-1} sec^{-1}	ν_{CO}, cm^{-1}[a]
$P(OCH_2)_3CCH_3$	0.008	0.109	15.4	1.4×10^{-4}	1979
$P(OCH_2)_3CCH_3$	0.008	0.200	28	1.4×10^{-4}	
$P(OC_6H_5)_3$	0.005	0.226	1.6	7.1×10^{-6}	1979
$p\text{-}CH_3C_6H_4NC$	0.005	0.230	390	1.7×10^{-3}	1973
$p\text{-}CH_3C_6H_4NC$	0.005	0.198	310	1.6×10^{-3}	
$C_6H_{11}NC$	0.005	0.148	2.6	1.8×10^{-5}	1960
$C_6H_{11}NC$	0.005	0.303	5.0	1.7×10^{-5}	
PR_3	0.005	0.3	Very slow		b

[a] The C–O stretching frequencies for C_5H_5RhCOL in toluene solution. [b] Phosphine derivatives showed no detectable reaction after days. The ν_{CO} for these varied from 1936 to 1942 cm^{-1}.

The nmr spectra data of some of the substitution products are collected in Table VI.

Discussion

The rate of reaction of $C_5H_5Rh(CO)_2$ with $P(C_6H_5)_3$ is approximately 10 times greater than that for the analogous cobalt or iridium compound (Table I). Qualitative observations[19] have been made which indicate that compounds of this type of the second-row transition metals are often more reactive than the corresponding compounds of the first- and third-row transition elements. Quantitative data on the rates of carbon monoxide exchange and of substitution reactions with $M(CO)_6$ show that molybdenum hexacarbonyl reacts more rapidly than do either the chromium or tungsten hexacarbonyls.[4] This result parallels the M–C stretching force constants for the hexacarbonyls, which have values of 2.03, 1.81, and 2.15 mdynes/A for M = Cr, Mo, and W, respectively.[20] Similarly, the C–O stretching bands of $C_5H_5Rh(CO)_2$ occur at higher frequencies than do the corresponding bands for the analogous cobalt and iridium compounds (Table I). This suggests that there is greater C–O multiplet bond character and consequently less M–C π bonding in the rhodium system than in the cobalt and iridium compounds. Because of its weaker M–C bond strength, the rhodium compound is the most reactive. This, unfortunately, does not answer the very puzzling question of why the Rh–C bond strength is the weakest in this triad nor why Mo–C is the weakest in its triad of hexacarbonyls. This appears to be an anomaly for which there is at present no adequate explanation.

Since π-cyclopentadienyl takes the place of three molecules of carbon monoxide in metal carbonyls, it follows that there is a formal analogy between com-

(19) R. B. King, *Advan. Organometal. Chem.*, **2**, 177 (1964).

(20) L. H. Jones, "Theory and Structure of Complex Compounds," B. Jezowska-Trzebiatowska, Ed., Pergamon Press, London, 1964, pp 45–53.

Table VI. Proton Nmr Data[a]

Compound	C5H5 protons Δ, ppm	Shape	J_{RhCH}, cps	J_{PRhCH}, cps	Ligand protons Δ, ppm	Shape	J_{POCH},[b] cps
C5H5RhCOPPh3	5.28	[1:2:1]	0.55	0.55	7.33 in CCl4	Split	
C5H5RhCOP(n-C4H9)3	5.41	triplet	0.55	0.55	1.51 / 1.08	Split	
C5H5RhCOP(OCH2)CCH3	5.51	Double doublet	0.6	1.2	3.70 / −0.17	Doublet / Singlet	5
C5H5RhCOP(OCH3)3	5.44		0.6	1.2	3.49	Doublet	13
C5H5Rh[P(OCH2)3CCH3]2	5.81	Triple [1:2:1] doublet	0.6	1.2	3.89 / −0.09	Triplet / Singlet	5
C5H5Rh[P(OCH3)3]2	5.59		0.6	1.2	3.60	Triplet	12.4
C5H5RhCOCNC6H11	5.48	Doublet	0.6	...	1.37 / 1.08	Split	
C5H5Rh(CO)2	5.12	Doublet	0.7	...	...		
C5H5CoCOP(C6H5)3	4.60	Doublet		1.0	7.0 / 7.6 in C6D6	Split	

[a] Measurements made on benzene solutions at 60 Mc. Δ values measured vs. C6H6, with Δ = 7.33 ppm downfield from TMS. [b] Or separation of outer peaks, respectively.

pounds of the types C5H5M(CO)2, where M = Co, Rh, and Ir, and M(CO)5, where M = Fe, Ru, and Os. Studies on C5H5Co(CO)2 indicate that its chemistry often resembles that of iron pentacarbonyl.[21] However, striking differences have also been observed. For example, the exchange of carbon monoxide with Fe(CO)5 is extremely slow,[22] whereas with C5H5Co(CO)2 it is fairly rapid.[6] The suggestion was made[6] that this might be due to the comparative ease with which a pair of electrons can transfer to the cyclopentadienyl ring and make available a vacant orbital on cobalt of relatively low energy. This could then accept a pair of electrons from the entering reagent and facilitate a nucleophilic displacement reaction.

Ample support is provided by the data in Tables II and III for a bimolecular displacement mechanism for substitutions in C5H5Rh(CO)2. Because of the nature of the bonding of the π-cyclopentadienyl group in this compound, the approach of a nucleophile with a lone pair of electrons may cause a pair of electrons from the metal (or metal–ligand bond) to concentrate on the ligand to form C5H5⁻. This would make the metal more positive, perhaps with an empty bonding orbital, and facilitate nucleophilic attack. A simple representation of this is shown by

$$(3)$$
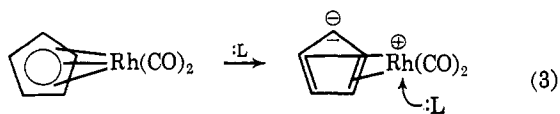
Rate constants for the reaction of C5H5Rh(CO)2 with various phosphines and phosphites are collected in Table III. Under these same conditions the compound shows no detectable reaction with either pyridine or triphenylarsine over a period of 1 week. This difference in behavior between the phosphorus ligand atom reagents and nitrogen or arsenic ligand atom reagents is in accord with the metal in the substrate being a class b[23] or soft[24] metal. Stability data for metal complexes

of class b metals show that for the group V elements, phosphorus compounds form the most stable metal complexes and the stabilities vary in the order N << P > As > Sb.

The results obtained indicate that phosphines displace CO from C5H5Rh(CO)2 more rapidly than phosphites. Since phosphites are better π bonders in these systems than are phosphines,[2,25] it follows that the π-bonding tendency of a reagent is not a predominant factor in determining its reactivity. Thorsteinson[26] has observed that the rates of reaction of CoNO(CO)3 with phosphine and phosphites increase with increasing basicity of the reagent. This same correlation is found for the reaction of C5H5Rh(CO)2, as is shown by the linear free energy relationship between the rate of reaction and the basicity of the reagent (Figure 1). The relative basicities of the reagents were measured by Streuli[18] using nitromethane as a solvent and recording the difference in half-neutralization potentials, ΔHNP, from that of N,N'-diphenylguanidine taken as a standard. That tricyclohexylphosphine reacts much slower than would be predicted by its basicity can be attributed to steric effects caused by the methylene groups adjacent to phosphorus of the cyclohexyl rings. In contrast to this, the relatively small steric requirement of P(OCH2)2CCH3 is perhaps responsible for its reacting faster than does P(n-OC4H9)3, although they may be of comparable base strengths.

This parallism between reagent reactivity and base strength is restricted to the phosphorus ligand atom compounds investigated. It is not correct to conclude that the stronger the base strength of a nucleophile, the better reagent it will be toward C5H5Rh(CO)2. The base strength of pyridine is larger than that of some of the phosphorus compounds, but yet pyridine is a much poorer reagent. Alternatively, the formation constants for silver(I) complexes show that pyridine is a much weaker base toward this class b metal ion than is triphenylphosphine.[27] This is perhaps due to the fact that nitrogen is much less polarizable than is phosphorus

(21) R. B. King, P. M. Treichel, and F. G. A. Stone, J. Am. Chem. Soc., 83, 3593, 3600 (1961).

(22) D. F. Keeley and R. E. Johnson, J. Inorg. Nucl. Chem., 11, 33 (1959).

(23) S. Ahrland, J. Chatt, and N. R. Davies, Quart. Rev. (London), 12, 265 (1958).

(24) R. G. Pearson, J. Am. Chem. Soc., 85, 3533 (1963).

(25) W. D. Horrocks, Jr., and R. C. Taylor, Inorg. Chem., 2, 723 (1963), and references therein.

(26) E. M. Thorsteinson, private communication.

(27) L. G. Sillén and A. E. Martell, "Stability Constants of Metal-Ion Complexes," Special Publication No. 17, The Chemical Society, London, 1964, pp 440, 721.
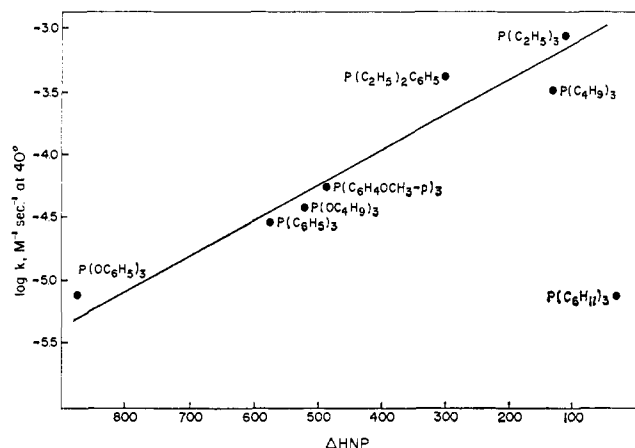
Figure 1. The linear free energy relationship of the rate of reaction with the polarizability of the nucleophile for the reaction of C_5H_5Rh-$(CO)_2$ with different reagents (see text for discussion that ΔHNP measures basicity which is believed to parallel polarizability for these phosphorus compounds).

and suggests that this is the important parameter in determining the nucleophilic strength of the reagent toward this substrate. Such a result seems plausible, for it is known that the nucleophilic strength of a reagent toward the class b or soft metal Pt(II) is dependent on the polarizability of the reagent and not its basicity.[28] Unfortunately, data on the polarizability of phosphorus in the reagents used are not available. However, it seems reasonable to assume that for this series of analogous compounds, the polarizability of phosphorus will parallel the basicity of the compound. Therefore, it would seem more reasonable to think of the correlation shown in Figure 1 as one with the polarizability of the nucleophile rather than its basicity.

The activation parameters for the reaction of C_5H_5-$Rh(CO)_2$ with $P(C_2H_5)_2C_6H_5$ and $P(n\text{-}OC_4H_9)_3$ in different solvents are shown in Table IV. The data reveal that the greater reactivity of $P(C_2H_5)_2C_6H_5$ is due to a decrease in the activation enthalpy. Negative entropies of activation are in accord with a bimolecular displacement process in which there is considerable bond formation with the entering reagent in the transition state. This increase in coordination number restricts the motion in the activated complex relative to the reactant molecules, resulting in a decrease in entropy. The effect of solvent is small.

The reactions described above are for the replacement of one carbon monoxide from $C_5H_5Rh(CO)_2$, as shown by eq 1. Under the conditions of our experiments there is no indication that the phosphines react beyond this stage. However, both phosphites and isonitriles readily replace also the second molecule of carbon monoxide by reaction 2. A similar behavior was reported[29] for the reaction of acylcobalt tetracarbonyls with phosphite esters compared to the reaction with triphenylphosphine. This result can be explained on the basis of the greater π-bonding tendency of the phosphites and isonitriles compared to the phosphines. Because of this there is less rhodium-to-carbon π bonding of the remaining CO in C_5H_5RhCOL, owing

to the competition with the π-bonding ligands L. This is supported by the infrared spectra which show a higher CO stretching frequency for compounds where L is a phosphite or isonitrile than where it is a phosphine. The data in Table V also show that this replacement of the last carbon monoxide is a second-order process.

The rate of replacement of the second carbon monoxide is always less than that for the replacement of the first. This difference is very large for the reaction with phosphines where the second step is immeasurably slow at the conditions of these experiments. However, the reaction of $C_5H_5Rh(CO)_2$ with $P(OCH_2)_3CCH_3$ is only four times faster than its reaction with C_5H_5Rh-$COP(OCH_2)_3CCH_3$. Reliable data could not be obtained for the replacement of the first carbon monoxide with the isonitriles. However, it is of interest to note that the rate of replacement of the second carbon monoxide is faster for the p-tolylisonitrile system than for the cyclohexylisonitrile. This is in accord with the p-tolylisonitrile being a better π bonder, which in turn means less Rh–C multiple bonding and greater reactivity than for the cyclohexylisonitrile system. The C–O stretching frequencies of the isonitrile derivatives support this conclusion. That the slowest second step is found for the reaction of $C_5H_5RhCOP(OC_6H_5)_3$ with $P(OC_6H_5)_3$ may be due to its being a poorer reagent and also to steric hindrance in this system which would make more difficult a bimolecular displacement process.

Attempts to measure the exchange of carbon monoxide with $C_5H_5Rh(CO)_2$ were not successful. The results obtained were not reproducible. The rates of exchange were faster for toluene solutions of the compound that had been aged at room temperature in the dark for a few days. Freshly prepared solutions did not give linear log plots of the data, but there was always a curvature indicating an increase in rate of exchange with time. These results suggest the formation of a catalyst in solution and it is known that the compound does lose carbon monoxide and form a dimer in solution.[30] The dimer was prepared and added to a solution of $C_5H_5Rh(CO)_2$ and found to have little effect on its rate of exchange. Although this dimer is not the catalyst, some other unknown substance can be present in catalytic amounts. Whatever this is, it does not appear to affect the substitution reactions. Perhaps in the substitution reactions the catalyst reacts with the excess reagent and is converted into an inactive substance.

Finally, the proton nmr spectral data for some of the compounds isolated are collected in Table VI. The rather remarkable feature of these spectra is the strong ^{31}P–^{31}P coupling observed for the disubstituted derivatives. This type of coupling is usually observed only with systems where the phosphorus atoms are in trans positions. For example, a 1:2:1 triplet was observed for trans-$Pd(P(CH_3)_2C_6H_5)_2I_2$, whereas only a doublet is observed for the cis isomer.[31] The two phosphite ligands in $C_5H_5RhL_2$ cannot occupy trans positions, but the nmr results show efficient phosphorus–phosphorus coupling. This result is similar to that

(28) J. O. Edwards and R. G. Pearson, J. Am. Chem. Soc., 84, 16 (1962); U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson, and A. Turco, ibid., 87, 241 (1965).

(29) R. F. Heck, J. Am. Chem. Soc., 85, 1220 (1963); 87, 2572 (1965).

(30) O. S. Mills, private communication; E. O. Fischer and K. S. Brenner, private communication; see also E. O. Fischer and K. Bittler, Z. Naturforsch., 16b, 835 (1961).

(31) J. M. Jenkins and B. L. Shaw, Proc. Chem. Soc., 279 (1963).

reported[32] for the tetrahedral systems $NiCOL_3$ and NiL_4 and suggests that strong P–P coupling may occur without the phosphorus atoms being in *trans* positions. The increase in the P–H coupling constant for $PRhC_5H_5$ in going from compounds containing phosphine ligands to those with phosphite ligands (Table VI) also suggests

a difference of bonding with rhodium between these two types of ligands.

Acknowledgment. This research is supported by National Science Foundation Grant GP-2505 to Northwestern University and the Technischen Hochschule, München. We wish to thank Professor E. O. Fischer for helpful suggestions and interest in this research.

(32) J. G. Verkade, R. E. McCarley, D. G. Henricker, and R. W. King, *Inorg. Chem.*, **4**, 228 (1965).

The Iron(III)-Catalyzed Oxidation of Cysteine by Molecular Oxygen in the Aqueous Phase. An Example of a Two-Thirds-Order Reaction
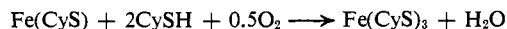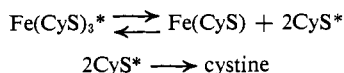
Jay E. Taylor, Johnson F. Yan, and Jin-liang Wang

Contribution from the Department of Chemistry, Kent State University, Kent, Ohio. Received November 8, 1965

Abstract: A careful investigation of the iron(III)-catalyzed oxidation of cysteine has demonstrated that the reaction is zero order with respect to both cysteine and oxygen but two-thirds order with ferric ion. There is a marked pH effect with a pronounced maximum in rate at pH 8.1, and the existence of an iron–cysteine complex has been well documented. A quantitative interpretation of these observations leads to the following proposal.

$$Fe^{3+} + 3CySH \rightleftharpoons Fe(CyS)_3 + 3H^+$$
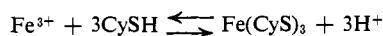
The $Fe(CyS)_3$ may undergo ionization due to the carboxyl and amino groups on the ligand, cysteine. One of the ionic forms is assumed to be specially reactive and is so designated as $Fe(CyS)_3^*$. The equilibria with the ionic forms of lesser activity on each side of the pH maximum explain the pH dependency of the reaction.

$$Fe(CyS)_3^* \rightleftharpoons Fe(CyS) + 2CyS^*$$

$$2CyS^* \longrightarrow cystine$$

$$Fe(CyS) + 2CySH + 0.5O_2 \longrightarrow Fe(CyS)_3 + H_2O$$

The second and last steps can be altered in different ways giving modifications which yield the same basic mathematical rate expression. The CyS* represents an intermediate which combines with itself to form cystine. There is not sufficient information available to attempt to define the nature of the CyS* intermediate. It may be a radical, an ionic species, a combination of activated units, or a molecular species of unusual reactivity. Since both cysteine and oxygen are in excess to the ferric ion concentration, the reason for the zero order in each case is obvious from the first and last steps. The two-thirds order in Fe^{3+} arises from the second and third steps. This mechanism gives a mathematical expression which very adequately correlates all of the presently known rate data. Obviously this proposal is not conclusive; however, if the actual mechanism is not as described above, it must give the same mathematical model.

The determination of the rate of the oxidation of cysteine by the method of measuring oxygen uptake has been the subject of various investigations. These were generally done at an early date and were of a low order of accuracy. A consistent evaluation of the rate data in terms of a valid mechanism does not appear in the literature. Among the investigations which have been made, Gerwe[1] found that pure cysteine, free from iron, is oxidized at a very slow rate; Mathews and Walker[2] reported that cysteine is oxidized in alkaline but not in acidic solutions. They also found that at 20° the maximum rate is reached at pH 8 and concluded that only the neutral nonionized molecule of cysteine oxidizes rapidly. The more rapid oxidation of

cysteine in the presence of cystine was noted by Abderhalden and Wertheimer.[3] The influence of various catalysts was systematized. The most recent study on this oxidation is probably that by Robert,[4] who reported the influence of copper on the oxidation of cysteine in alkaline solutions. A brief review has been made by Tarbell.[5]

In most of the works mentioned above, experiments were conducted in vessels shaken vigorously and connected to an air or oxygen source, and the whole system was kept airtight. The decrease in a mercury barometer was recorded as a measure of the amount of

(1) E. G. Gerwe, *J. Biol. Chem.*, **92**, 399 (1931).
(2) A. P. Mathews and S. Walker, *ibid.*, **6**, 21, 289 (1909).

(3) E. Abderhalden and E. Wertheimer, *Arch. Ges. Physiol.* (Pflüger's), **197**, 131 (1922); **199**, 336 (1923).
(4) C. Robert, *Bull. Soc. Chim. Biol.*, **36**, 253 (1954).
(5) D. S. Tarbell, "Organic Sulfur Compounds," Vol. I, N. Kharasch, Ed., Pergamon Press, New York, N. Y., 1961, p 97.