anions. The Cl 2p binding-energy spectra of the two chloride complexes are each characterized by a very well-resolved Cl $2p_{1/2,3/2}$ doublet (the Cl $2p_{3/2}$ component is located at 198.2 eV for $W_2Cl_4(OMe)_2(MeOH)_4$ and 197.9 eV for $W_2Cl_4(OEt)_2(EtOH)_4$) which is a good indication that only a single type of chlorine environment[25] is present within these complexes. This supports an alkoxy-bridged structure rather than a halogen-bridged structure for $W_2X_4(OR)_2(ROH)_4$.

Acknowledgment. Support from the National Science Foundation (Grants CHE74-12788 and CHE79-09233) is gratefully acknowledged.

Registry No. $Mo_2(mhp)_4$, 67634-80-4; $W_2(mhp)_4$, 67634-84-8; $Cs_4Mo_2Cl_8$, 55937-61-6; $Cs_4Mo_2Br_8$, 41772-62-7; $[Bu_4N]_2Mo_4I_{11}$, 68024-65-7; $Cs_3W_2Cl_9$, 23403-18-1; $Cs_3W_2Br_9$, 72332-25-3; $W_2Cl_4(OMe)_2(MeOH)_4$, 12552-15-7; $W_2Br_4(OMe)_2(MeOH)_4$, 72301-56-5; $W_2Cl_4(OEt)_2(EtOH)_4$, 72301-57-6.

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Reactions of Metal Carbonyl Derivatives. 23.[1] Donor Behavior of $[FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_4R)]$ (R = H, CH_3) toward Various Rhodium and Iridium Complexes and the Role of the Solvent in the Type of Product Formed. Reversible Uptake of Carbon Monoxide and Dihydrogen by the Nonclosed Trinuclear Species $[M'\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_4R)\}_2]^+$ (M′ = Rh, Ir)[2]

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The metal-containing phosphine $[P(C_6H_5)_2ML_n]$ ($ML_n = Fe(CO)_2(\eta\text{-}C_5H_4R)$ (R = H or CH_3)) reacts with various compounds of rhodium in alcohol, including $[RhCl_3\cdot 3H_2O]$ and $[\{Rh(C_8H_{12})Cl\}_2]$, to produce in each case, when present in slight excess, a cationic species of stoichiometry $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_4R)\}_2]^+$, having a nonclosed structure in which the iron and rhodium atoms are bridged by a carbonyl as well as by a phosphino group. The iridium analogue is formed in the corresponding reaction involving $[Ir(C_8H_{12})(solvent)_x]^+$ but not $[\{Ir(C_8H_{12})Cl\}_2]$. Coordinating solvents such as tetrahydrofuran, acetone, diglyme, methanol, and acetonitrile react reversibly with these cationic species to afford products containing terminal carbonyls only. Controlled addition of $P(OCH_3)_3$, $P(C_6H_5)_3$, halide ions, or pseudohalide ions to $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_4R)\}_2]^+$ leads to the formation of simple adducts of the parent compound, in which the bridged structure is retained, while treatment of $[M'\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_4R)\}_2]^+$ (M′ = Rh, Ir) with carbon monoxide in dichloromethane or chloroform gives rise to a compound characterized as $[M'(CO)_3\{P(C_6H_5)_2ML_n\}_2]^+$. Whereas the carbonylation of $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_4R)\}_2]^+$ is reversible, that involving the iridium species is irreversible. Hydrogen also reacts with $[M'\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_4R)\}_2]^+$ although high pressures are required for the rhodium reaction. Treatment of $[\{Rh(CO)_2Cl\}_2]$ or $[\{Rh(C_8H_{12})Cl\}_2]$ with $[P(C_6H_5)_2ML_n]$ in benzene affords neutral $[Rh(CO)\{P(C_6H_5)_2ML_n\}_2Cl]$ which can be converted to $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_4R)\}_2]^+$ by treatment with silver ions. The iridium compound $[Ir(CO)\{P(C_6H_5)_2ML_n\}_2Cl]$ is obtained similarly from $[\{Ir(C_8H_{12})Cl\}_2]$. Reaction of $[RhL'_2(solvent)_x]^+$ or $[Rh(C_8H_{12})L'_2]^+$ ($L' = P(OC_6H_5)_3$, $P(CH_3)_2C_6H_5$; $2L' = C_8H_{12}$ or $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$) with an equimolar amount of $[P(C_6H_5)_2ML_n]$ in alcohol gives a dinuclear product, $[RhL'_2\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}]^+$, which, similar to the trinuclear species, contains both a bridging carbonyl and a bridging phosphino group. The donor properties of $[SR'ML_n]$ ($R' = C_2H_5$, $t\text{-}C_4H_9$, C_6H_5) toward various rhodium derivatives are also described.

Metal-cluster complexes are receiving much attention of late. This can be attributed to their potential as models for metal surfaces in heterogeneous catalysis[4,5] as well as to the highly fascinating and novel chemistry already discovered for a number of them.[4-12] Support for their utilization as models is provided by recent observations that certain metal-cluster derivatives are effective homogeneous catalysts for a number of processes which, until these particular discoveries, could only be catalyzed by heterogeneous systems. For instance $[Os_3(CO)_{12}]$ and $[Ir_4(CO)_{12}]$ have been found to homogeneously catalyze the reduction of carbon monoxide by dihydrogen to methane,[13] a reaction readily promoted by nickel surfaces[14] and for which mononuclear homogeneous catalysts have thus far not been reported.[15] Furthermore ruthenium and mixed iron/ruthenium carbonyl clusters, in the presence of a base,

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[15] Recent studies[16,17] have revealed that mononuclear carbonyl and hydride complexes of bis(pentamethylcyclopentadienyl)zirconium are capable of promoting the stoichiometric reduction of carbon monoxide by dihydrogen to methoxide but a dinuclear species $[\{Zr\{\eta\text{-}C_5(CH_3)_5\}_2H\}_2CH_2O]$ has been proposed as an intermediate in this reaction.[17] Significantly a compound analogous to this intermediate, viz., $[\{Zr(\eta\text{-}C_5H_5)_2Cl\}_2CH_2O]$, has been shown to be produced in the reaction of $[Zr(\eta\text{-}C_5H_5)_2HCl]$ with carbon monoxide.[18]

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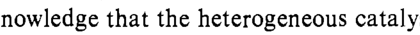
have been shown to effect the water gas shift,[19-21] a process normally associated with heterogeneous catalytic systems.[22,23]

Mixed-metal clusters containing main group as well as transition metals could well have wider application as homogeneous catalysts than homonuclear systems, particularly for those processes involving the reduction of carbon monoxide and other triple-bonded molecules such as dinitrogen, by dihydrogen, in that the dissimilar metal atoms in these compounds will not only function as ligands for each other but will have the potential of (i) binding to both ends of a substrate, e.g., carbon monoxide, and thereby increasing the activation of that species and (ii) activating two very different substrates at adjacent metal sites. Some recent studies involving the catalytic hydrogenation of carbon monoxide by $[Ir_4(CO)_{12}]$ support these views.[27]

In the knowledge that the heterogeneous catalyst utilized in the Fischer–Tropsch process for the production of hydrocarbons from synthesis gas is derived from iron and that rhodium has provided a number of very active homogeneous catalysts, a project was initiated with the aim of synthesizing rhodium–iron clusters and of studying their behavior toward carbon monoxide and hydrogen. The method of synthesis chosen involved the reaction of iron-containing phosphines with appropriate rhodium complexes. This paper reports the results of a study using $[FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_4R)]$ (R = H or CH_3) as ligand.

Results and Discussion

It is well documented that treatment of $[\{Rh(CO)_2Cl\}_2]$ with excess $P(C_6H_5)_3$ in benzene or ethanol leads to cleavage of the chlorine bridges and the formation of neutral *trans*-$[Rh(CO)\{P(C_6H_5)_3\}_2Cl]$ in high yield.[28-31] It is thus not surprising that the reaction of this rhodium dimer with the metal-containing phosphine $[FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_4R)]$ (R = H or CH_3) in benzene afforded, in good yield, an analogous product characterized as $[Rh(CO)\{P(C_6H_5)_2ML_n\}_2Cl]$ ($ML_n = Fe(CO)_2(\eta\text{-}C_5H_4R)$) (I: M′ = Rh; R = H, CH_3). This compound, which separated from the reaction mixture as a yellow air-unstable microcrystalline solid, was also isolated from the corresponding reaction involving $[\{Rh(C_8H_{12})Cl\}_2]$ but the yield was much lower. When the latter reaction was carried out in toluene at −80 °C, a green reaction mixture, which afforded an infrared spectrum with C–O stretching peaks at 1960 (s) and 1797 (s) cm^{-1} (measured in CH_2Cl_2), was obtained. Warming this green solution to room temperature again produced $[Rh(CO)\{P(C_6H_5)_2ML_n\}_2Cl]$ (I: M′ = Rh; R = H, CH_3) indicating that the green compound is an intermediate in the formation of the latter from $[\{Rh(C_8H_{12})Cl\}_2]$ and $[P(C_6H_5)_2ML_n]$. These products contrast with those formed in the corresponding reaction involving $P(C_6H_5)_3$ which affords $[Rh(C_8H_{12})\{P(C_6H_5)_3\}Cl]$ or $[Rh\{P(C_6H_5)_3\}_3Cl]$ depending on the $[\{Rh(C_8H_{12})Cl\}_2]/P(C_6H_5)_3$ molar ratio.[32-34] $[Ir(CO)\{P(C_6H_5)_2ML_n\}_2Cl]$ (I: M′ = Ir; R = H, CH_3) was synthesized analogously to $[Rh(CO)\{P(C_6H_5)_2ML_n\}_2Cl]$ (I: M′ = Rh; R = H, CH_3) from $[\{Ir(C_8H_{12})Cl\}_2]$ and $[P(C_6H_5)_2ML_n]$ but attempts to obtain $[Rh(CO)\{S(C_6H_5)ML_n\}_2Cl]$ by reaction of $[\{Rh(CO)_2Cl\}_2]$ with $[FeS(C_6H_5)(CO)_2(\eta\text{-}C_5H_5)]$ in benzene proved unsuccessful. $[\{Rh(CO)_2SC_6H_5\}_2]$ and $[Fe(\eta\text{-}C_5H_5)(CO)_2Cl]$, resulting from simple metathesis, were found to be formed instead.



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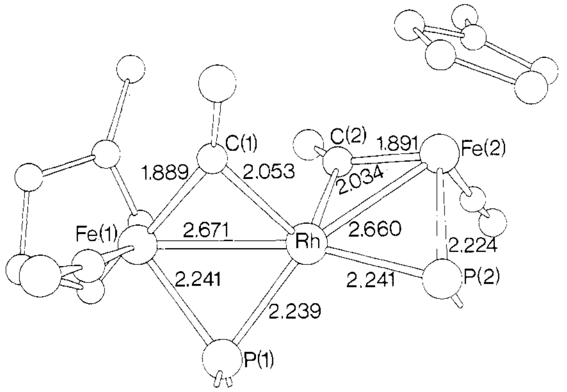

Figure 1. Stereochemistry of $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_4CH_3)\}_2]^+$ about the rhodium atom. Reprinted with permission from ref 2a. Copyright 1972 The Chemical Society, London.

The solid-state and carbon tetrachloride solution infrared spectra of $[M'(CO)\{P(C_6H_5)_2ML_n\}_2Cl]$ (I: M′ = Rh, Ir; R = H) reveal very similar band patterns in the C–O stretching region with the former being slightly better resolved. Peak frequencies are recorded in Table I. On the basis of the C–O stretching frequencies for *trans*-$[M'(CO)\{P(C_6H_5)_3\}_2Cl]$ (M′ = Rh, Ir)[30,35] the four highest energy bands in the solid-state spectra and the three highest in the CCl_4 solution spectra are assigned to the carbonyl groups bonded to the two iron atoms while the lowest energy peak is assigned to the carbonyl coordinated to the rhodium or iridium. Both $[Rh(CO)\{P(C_6H_5)_2ML_n\}_2Cl]$ and $[Ir(CO)\{P(C_6H_5)_2ML_n\}_2Cl]$ are assumed to have a trans configuration, as illustrated (I), similar to that found for $[M'(CO)\{P(C_6H_5)_3\}_2Cl]$ (M′ = Rh or Ir).[29,35]

While, as described above, the reaction of $[\{Rh(C_8H_{12})Cl\}_2]$ with $P(C_6H_5)_3$ in benzene affords neutral products only, treatment of this rhodium dimer with a fourfold molar amount of this ligand in ethanol or methanol in the presence of a suitable counterion leads to the formation of a cationic species, viz., $[Rh(C_8H_{12})\{P(C_6H_5)_3\}_2]^+$.[36,37] The reaction of $[\{Rh(C_8H_{12})Cl\}_2]$ with a slight excess of $[P(C_6H_5)_2ML_n]$ in ethanol in the presence of $[B(C_6H_5)_4]^-$, $[PF_6]^-$, or $[SbF_6]^-$ was also found to produce an ionic compound, which separated from solution as a red crystalline solid, but elemental analysis indicated its stoichiometry to be $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}$

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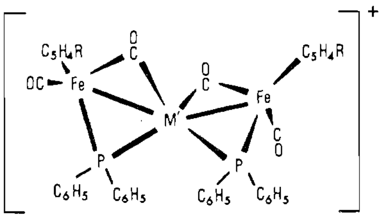
Table I. Infrared Spectroscopic Data

compd	C–O stretching freq, cm^{-1}
$[FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)]$	2015 (s), 1966 (s)[a]
$[FeS(C_2H_5)(CO)_2(\eta\text{-}C_5H_5)]$	2030 (s), 1979 (s)[b]
$[FeS(t\text{-}C_4H_9)(CO)_2(\eta\text{-}C_5H_5)]$	2027 (s), 1975 (s)[b]
$[FeS(C_6H_5)(CO)_2(\eta\text{-}C_5H_5)]$	2035 (s), 1986 (s)[b]
$[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}(C_8H_{12})][SbF_6]$	2013 (s), 1834 (ms)[b]
	2010 (s), 1830 (s)[c]
$[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}\{P(CH_3)_2C_6H_5\}_2][SbF_6]$	1995 (s), 1827 (m)[b]
	1985 (s), 1810 (ms)[c]
$[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}\{P(OC_6H_5)_3\}_2][SbF_6]$	2028 (s), 1850 (m)[b]
	2024 (sh), 2017 (s), 1842 (w), 1822 (m)[c]
$[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}\{(C_6H_5)_2PC_2H_4P(C_6H_5)_2\}][SbF_6]$	2005 (s), 1824 (m)[b]
	1990 (s), 1807 (m)[c]
$[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2][PF_6]$	2013 (s), 1850 (m), 1821 (m)[b]
	2018 (m), 2002 (s), 1848 (m), 1822 (m)[c]
$[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2][SbF_6]$	2013 (s), 1850 (m), 1821 (m)[b]
	2004 (s), 1856 (m), 1820 (m)[c]
$[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2][B(C_6H_5)_4]$	2013 (s), 1850 (m), 1821 (m)[b]
	1998 (s), 1843 (m), 1817 (m)[c]
$[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_4CH_3)\}_2][PF_6]$	2004 (s), 1842 (m), 1813 (m)[b]
$[Ir\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2][SbF_6]$	2009 (s), 1829 (m), 1798 (m)[b]
	2002 (s), 1830 (ms), 1799 (m)[c]
$[Ir\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2][B(C_6H_5)_4]$	2009 (s), 1829 (m), 1798 (m)[b]
	1996 (s), 1822 (m), 1796 (m)[c]
$[Rh\{FeS(t\text{-}C_4H_9)(CO)_2(\eta\text{-}C_5H_5)\}_2][SbF_6]$	2026 (s), 1868 (m), 1836 (m)[b]
	2007 (s), 1857 (m), 1827 (m)[c]
$[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2(solvent)_x][SbF_6]$	2024 (s), 1970 (s), 1960 (ip)[d]
	2022 (s), 1974 (s), 1960 (ip)[e]
	2020 (s), 1968 (s), 1959 (ip)[f]
	2025 (s), 1977 (s), 1940 (ip)[g]
	2026 (s), 1981 (s), 1952 (ip)[h]
$[Ir\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2(solvent)_x][B(C_6H_5)_4]$	2026 (s), 1970 (s), 1950 (sh)[d]
	2025 (s), 1972 (s), 1945 (sh)[e]
	2023 (s), 1970 (s), 1950 (sh)[f]
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3S(C_2H_5)][B(C_6H_5)_4]$	2034 (s), 2009 (m, sh), 1845 (m)[b]
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3S(t\text{-}C_4H_9)][B(C_6H_5)_4]$	2030 (s), 2003 (m, sh), 1842 (m)[b]
$[Rh\{FeS(C_6H_5)(CO)_2(\eta\text{-}C_5H_5)\}_2(C_8H_{12})][SbF_6]$	2051 (s), 2006 (s)[b]
	2058 (s), 1997 (s)[i]
$[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2\{P(OCH_3)_3\}][B(C_6H_5)_4]$	1997 (s), 1823 (ms), 1796 (ms)[b]
	1987 (s), 1812 (ms), 1788 (ms)[c]
$[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2\{P(C_6H_5)_3\}][B(C_6H_5)_4]$	2002 (s), 1806 (ms)[b]
	1988 (s), 1801 (s)[i]
$[Rh(CO)_3\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2][PF_6]$	2037 (s), 1996 (s), 1987 (s)[b]
	2038 (s), 2012 (s), 1990 (s)[c]
$[Rh(CO)_3\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2][SbF_6]$	2037 (s), 1996 (s), 1988 (s)[b]
	2039 (s), 2012 (s), 1990 (s)[c]
$[Rh(CO)_3\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2][B(C_6H_5)_4]$	2037 (s), 1996 (s), 1988 (s)[b]
	2026 (ms), 1995 (s), 1966 (ms)[c]
$[Ir(CO)_3\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2][B(C_6H_5)_4]$	2053 (sh), 2041 (s), 2003 (s), 1986 (sh), 1964 (sh)[b]
	2045 (sh), 2030 (s), 1994 (s), 1980 (sh), 1960 (sh)[c]
$[Rh(CO)\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2Cl]$	2027 (s), 1983 (sh), 1975 (s), 1949 (m)[j]
	2021 (s), 1972 (s), 1950 (ip)[b]
	2020 (ms), 2018 (sh), 1980 (ms), 1967 (s), 1948 (s)[c]
$[Rh(CO)\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_4CH_3)\}_2Cl]$	2020 (s), 1968 (s), 1950 (ip)[b]
$[Ir(CO)\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2Cl]$	2022 (s), 1981 (s), 1967 (s), 1938 (s)[j]
	2025 (s), 1976 (s), 1944 (sh)[b]
	2023 (ms), 2018 (ms), 1980 (sh), 1969 (s), 1942 (ms)[c]
$[Ir(CO)\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_4CH_3)\}_2Cl]$	2025 (s), 1968 (s), 1938 (sh)[b]
$[Rh(CO)\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2Br]$	2026 (s), 1996 (s), 1976 (s), 1945 (s)[j]
$[Ir(CO)\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2Br]$	2025 (s), 1996 (m), 1976 (s), 1945 (m)[j]
$[Rh(CO)\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2I]$	2025 (s), 1997 (m), 1976 (s), 1945 (m)[j]
	2024 (s), 1972 (s), 1950 (ip)[b]
$[Rh(CO)\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_4CH_3)\}_2I]$	2024 (s), 1970 (s), 1950 (ip)[b]
$[Ir(CO)\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2I]$	2025 (s), 1997 (m), 1968 (s), 1944 (m)[j]
$[Rh(CO)\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2CN]$[k]	2027 (s), 1996 (ms), 1973 (s), 1946 (m)[j]
$[Ir(CO)\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2CN]$[k]	2027 (s), 1995 (m), 1973 (s), 1944 (m)[j]
$[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2Cl]$	1960 (s), 1797 (s)[b]
$[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2Br]$	1960 (s), 1795 (s)[b]
$[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2I]$	1955 (s), 1797 (s)[b]
$[Ir\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2I]$	1937 (s), 1779 (s)[b]
$[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2CN]$[k]	ca. 1970, 1830, 1804[b]

[a] Measured in cyclohexane. [b] CH_2Cl_2. [c] Nujol mull. [d] Tetrahydrofuran. [e] Acetone. [f] Diglyme. [g] Pyridine. [h] Acetonitrile. [i] KBr disk. [j] Carbon tetrachloride. [k] $\nu(CN) = 2100\ cm^{-1}$.

$C_5H_4R)\}_2][A]$ (A = $B(C_6H_5)_4$, PF_6, SbF_6). The same species was formed in the reaction of $[Rh(C_8H_{12})(THF)_x]^+$ (THF = tetrahydrofuran; x = 2, 3) with a twofold molar amount of $[P(C_6H_5)_2ML_n]$ in THF and on treatment of $[RhCl_3{\cdot}3H_2O]$, $[\{Rh(CO)_2Cl\}_2]$, $[\{Rh(\eta\text{-}C_3H_5)_2Cl\}_2]$, $[Rh(C_8H_{12})(C_6H_6)]^+$, or $[\{Rh(olefin)_2Cl\}_2]$ with this ligand in ethanol or methanol in the presence of a large counterion. The solid-state and dichloromethane and chloroform solution infrared spectra of this species contained a single terminal and two bridging carbonyl stretching peaks (see Table I) while the proton nuclear magnetic resonance spectra in CD_2Cl_2 exhibited peaks corresponding to phenyl, cyclopentadienyl, and for R = CH_3 methyl protons only. It was apparent from these spectroscopic data that the compound has an unusual structure and a single-crystal X-ray diffraction study was thus carried out on $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_4CH_3)\}_2][PF_6]$. The essential stereochemistry of the cation is illustrated in Figure 1. It has a nonclosed structure with the rhodium being bound to the iron atoms not only by bridging carbonyl and bridging phosphino groups but also through rhodium–iron bonds (Rh–Fe = 2.671 and 2.660 ± 0.002 Å). The three metal atoms are nonlinear (Fe(1)–Rh–Fe(2) bond angle = 145.0°) while the two FeCRhP rings are puckered (the Fe(1)C(1)Rh–Fe(1)P(1)Rh and Fe(2)C(2)Rh–Fe(2)P(2)Rh interplanar angles are 155.6 and 153.5° respectively), giving rise to a rather unusual stereochemistry about the rhodium. A more detailed description of the structure is given in a separate publication.[2,38]

The similar band patterns of the C–O stretching peaks in the solid-state and dichloromethane and chloroform solution infrared spectra of $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_4R)\}_2]^+$ indicate that the solid-state structure (II: M′ = Rh; R = H, CH_3) is retained in these solvents. The cation has symmetry C_2 and is thus chiral. The two phenyl groups associated with the same phosphorus atom are nonequivalent but rapid racemization would lead to all four phenyl groups becoming equivalent. The room-temperature proton nuclear magnetic resonance spectra of the above compounds in CD_2Cl_2 exhibited a single sharp resonance for the aromatic protons, but a recent variable-temperature study on $[Rh\{FeP(p\text{-}C_6H_4CH_3)_2(CO)_2(\eta\text{-}C_5H_5)\}_2]^+$ by Norton et al.[39] has shown that the aromatic peaks for this compound are very sensitive to temperature changes and at −50 °C can be described in terms of two partially overlapping AB patterns. A pathway involving coordination of the solvent to the rhodium has been proposed for this racemization, but alternative mechanisms not involving direct solvent participation cannot be eliminated.[39,40]

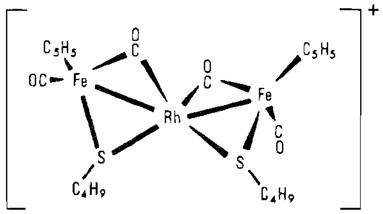


II

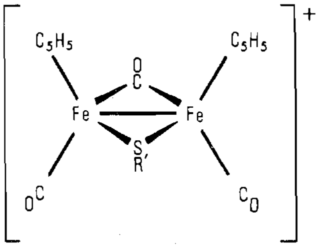
Significantly in a number of the syntheses of $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2]^+$ (II: M′ = Rh; R = H) from $[\{Rh(C_8H_{12})Cl\}_2]$, the reaction mixture, on warming from −80 to 0 °C, was observed to turn green prior to the precipitation of the final product. An infrared spectrum of this reaction mixture gave C–O stretching peaks at 1960 (s) and 1797 (s) cm^{-1} (measured in CH_2Cl_2) indicating that the green compound described earlier is an intermediate in this reaction.

Attempts to obtain $[Ir\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2][B(C_6H_5)_4]$ (II$[B(C_6H_5)_4]$: M′ = Ir; R = H) by reacting $[\{Ir(C_8H_{12})Cl\}_2]$ with a slight excess of $[FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)]$ in methanol in the presence of $Na[B(C_6H_5)_4]$ were unsuccessful and gave without exception the neutral compound $[Ir(CO)\{P(C_6H_5)_2ML_n\}_2Cl]$ (I: M′ = Ir; R = H). However, the hexafluoroantimonate salt of II (M′ = Ir; R = H) was isolated in low to moderate yield from the reaction of $[Ir(C_8H_{12})(THF)_x][SbF_6]$ with a twice molar amount of $[FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)]$ in tetrahydrofuran. A modification of this method involving the addition of $Na[B(C_6H_5)_4]$ to the reaction mixture produced by treating $[Ir(C_8H_{12})(ethanol)_x][BF_4]$ with an appropriate amount of $[FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)]$ in ethanol was found to give the highest yield of $[Ir\{FeP(C_6H_5)_2(\eta\text{-}C_5H_5)\}_2]^+$ (II: M′ = Ir; R = H).

A green cationic species, $[Rh\{FeS(t\text{-}C_4H_9)(CO)_2(\eta\text{-}C_5H_5)\}_2][SbF_6]$ (III$[SbF_6]$), was also isolated from the reaction of $[Rh(C_8H_{12})(ethanol)_x][SbF_6]$ with a slight excess of the metal-containing sulfide $[FeS(t\text{-}C_4H_9)(CO)_2(\eta\text{-}C_5H_5)]$ in ethanol. The presence of a single terminal and two bridging carbonyl stretching modes in the solid-state and dichloromethane infrared spectra of this compound indicated that it has a structure analogous to that of $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_4R)\}_2]^+$ (II: M′ = Rh; R = H, CH_3). $[Rh\{FeS(t\text{-}C_4H_9)(CO)_2(\eta\text{-}C_5H_5)\}_2]^+$ (III) was also obtained by treatment of $[\{Rh(C_8H_{12})Cl\}_2]$ with $[FeS(t\text{-}C_4H_9)(CO)_2(\eta\text{-}C_5H_5)]$ in methanol at −78 °C followed by the addition of $Na[B(C_6H_5)_4]$ to precipitate the product. A different product was isolated from this reaction when it was performed at room temperature. This was characterized as the dinuclear species $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3S(t\text{-}C_4H_9)][B(C_6H_5)_4]$ (IV$[B(C_6H_5)_4]$: R′ = $t\text{-}C_4H_9$). Compounds of this type have been synthesized previously by reacting $[Fe(\eta\text{-}C_5H_5)(CO)_2(solvent)]^+$ with $[FeSR'(CO)_2(\eta\text{-}C_5H_5)]$ (R′ = C_2H_5 or $t\text{-}C_4H_9$) in the presence of a suitable counterion.[42] $[FeS(C_2H_5)(CO)_2(\eta\text{-}C_5H_5)]$ was found to behave in a slightly different manner to $[FeS(t\text{-}C_4H_9)(CO)_2(\eta\text{-}C_5H_5)]$ in that it afforded $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3S(C_2H_5)][B(C_6H_5)_4]$ (IV$[B(C_6H_5)_4]$: R′ = C_2H_5) at a temperature of −80 °C as well as at ambient temperature.



III



IV

Treatment of $[Rh(C_8H_{12})(ethanol)_x][SbF_6]$ with $[FeS(C_6H_5)(CO)_2(\eta\text{-}C_5H_5)]$ in ethanol in a molar ratio of 1:2.5 was found not to afford $[Rh\{FeS(C_6H_5)(CO)_2(\eta\text{-}C_5H_5)\}_2][SbF_6]$ (III$[SbF_6]$: R′ = C_6H_5) or $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3S(C_6H_5)][SbF_6]$ (IV$[SbF_6]$; R′ = C_6H_5) but an orange crystalline derivative containing terminal carbonyls only. A nuclear magnetic resonance spectrum of this compound could not be

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(38) R. Mason and J. A. Zubieta, *J. Organomet. Chem.*, **66**, 279 (1974).

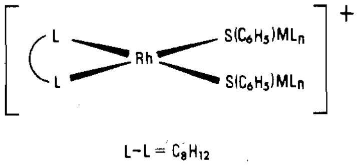
(39) A. Agapiou, S. E. Pedersen, L. A. Zyzyck, and J. R. Norton, *J. Chem. Soc., Chem. Commun.*, 393 (1977).

(40) The racemization of $[\{Mn(\eta\text{-}C_5H_4CH_3)(CO)_2\}_2S(C_2H_5)]^{+}$[41] is at present believed to occur by a mechanism not involving direct participation of the solvent.

(41) J. C. T. R. Burckett-St. Laurent, M. R. Caira, R. B. English, R. J. Haines, and L. R. Nassimbeni, *J. Chem. Soc., Dalton Trans.*, 1077 (1977).

(42) R. B. English, R. J. Haines, and C. R. Nolte, *J. Chem. Soc., Dalton Trans.*, 1030 (1975).

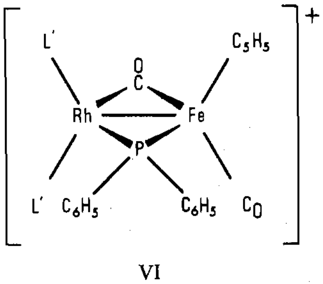
obtained, but on the basis of its elemental analysis and the presence of peaks in its solid-state infrared spectrum at 742 and 1430 cm^{-1}, assigned to coordinated C_8H_{12},[43] it was assumed to be $[Rh\{FeS(C_6H_5)(CO)_2(\eta\text{-}C_5H_5)\}_2(C_8H_{12})][SbF_6]$ ($V[SbF_6]$).



L–L = C_8H_{12}

V

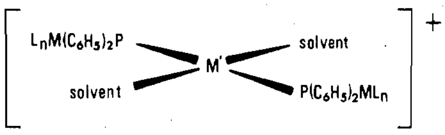
Controlled addition of $[FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)]$ to an equimolar quantity of $[Rh(C_8H_{12})(\text{ethanol})_x][SbF_6]$ in ethanol led to the formation of a di- and not a trinuclear product. This was characterized as $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}(C_8H_{12})][SbF_6]$. The presence of a bridging carbonyl as well as a terminal carbonyl stretching band in the infrared spectrum of this compound is consistent with the cation having structure VI ($2L' = C_8H_{12}$).



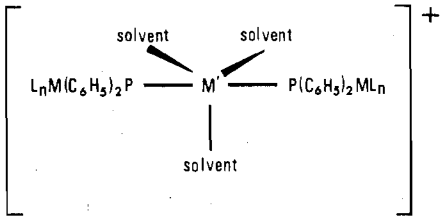
VI

A product with a similar structure, viz., $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}\{P(OC_6H_5)_3\}_2][SbF_6]$ ($VI[SbF_6]$: $L' = P(OC_6H_5)_3$) was obtained analogously from $[Rh\{P(OC_6H_5)_3\}_2(\text{ethanol})_x][SbF_6]$ while compounds of this type, viz., $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}(C_6H_5)_2PC_2H_4P(C_6H_5)_2][SbF_6]$ ($VI[SbF_6]$: $2L' = (C_6H_5)_2PC_2H_4P(C_6H_5)_2$) and $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}\{P(CH_3)_2C_6H_5\}_2][SbF_6]$ ($VI[SbF_6]$: $L' = P(CH_3)_2C_6H_5$), were also obtained from the reactions of $[FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)]$ with $[Rh\{(C_6H_5)_2PC_2H_4P(C_6H_5)_2\}(C_8H_{12})][SbF_6]$ and $[Rh\{P(CH_3)_2C_6H_5\}_2(C_8H_{12})][SbF_6]$, respectively. All of the above dinuclear species decompose in solution such that their nuclear magnetic resonance spectra could not be measured. Structural assignments were thus based on infrared evidence only.

Dissolution of $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_4R)\}_2]^+$ (II: $M' = Rh$; $R = H, CH_3$) in coordinating solvents such as acetone, diglyme, nitromethane, acetonitrile, or pyridine, and to a lesser extent tetrahydrofuran or methanol, gave red solutions which turned yellow with time. The decolorization was rapid for the stronger coordinating solvents but considerably slower for the weaker ones. Infrared spectral measurements on these yellow solutions indicated that the species present in solution contained terminal carbonyls only and that a rearrangement of the molecular framework had been effected (e.g., in THF, ν(C–O) = 2024 (s), 1970 (s), and 1960 (ip) cm^{-1}; in acetone, ν(C–O) = 2022 (s), 1974 (s), and 1960 (ip) cm^{-1}) (ip = inflection point). For the weaker coordinating solvents the process was reversible and evaporation of their solutions led to the recovery of the parent compound in near quantitative yield. It is apparent that the above dissolution process leads to the coordination of the solvent to the metal complex and the formation of a solvento species, $[Rh\{P(C_6H_5)_2ML_n\}_2(\text{solvent})_x]^+$ ($x = 2, 3$), with a structure presumed to be that represented by either VII or VIII, resulting from not only the conversion of the bridging carbonyl groups of II to terminal carbonyls but also the cleavage of the metal–metal bonds in this species.[44]



VII



VIII

The tetrahydrofuran, diglyme, and acetone spectra of $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_4R)\}_2]^+$ (II: $M' = Rh$; $R = H$) also afforded a number of weak peaks in the C–O stretching region, including one at ca. 1800 cm^{-1}. This peak, readily assigned to one or more bridging carbonyl groups, gained in intensity in the initial stages of the solvation process but disappeared from the spectrum on completion of the formation of $[Rh\{P(C_6H_5)_2ML_n\}_2(\text{solvent})_x]^+$. Tests conducted on solutions of $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2]^+$ (II: $M' = Rh$; $R = H$) established that the peak did not arise from chloride ion attack on $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2]^+$ by the infrared cell windows[45] and thus could well be due to the formation of a 1:1 solvent adduct of II, viz., $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2(\text{solvent})]^+$, with a structure based on that of its parent.

$[Ir\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2]^+$ (II: $M' = Ir$; $R = H$) and the dinuclear rhodium species $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}L'_2]^+$ (VI: $L' = P(OC_6H_5)_3$, $P(CH_3)_2C_6H_5$; $2L' = C_8H_{12}$, $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$) were also found to be susceptible to solvent attack with that involving $[Ir\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2]^+$ being reversible.

Addition of an equimolar quantity of $[N(C_4H_9)_4]Cl$ to $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2]^+$ (II: $M' = Rh$; $R = H$) in CH_2Cl_2 afforded a green reaction mixture from which a green solid product with C–O stretching peaks at 1960 (s) and 1797 (s) cm^{-1}, measured in CH_2Cl_2, could be isolated. This species which was shown to be neutral from conductivity measurements, was found to revert to $[Rh(CO)\{P(C_6H_5)_2ML_n\}_2Cl]$ (I: $M' = Rh$; $R = H$) in the solid state and thus could not be isolated sufficiently pure for characterization purposes. However, the observation that it is an intermediate

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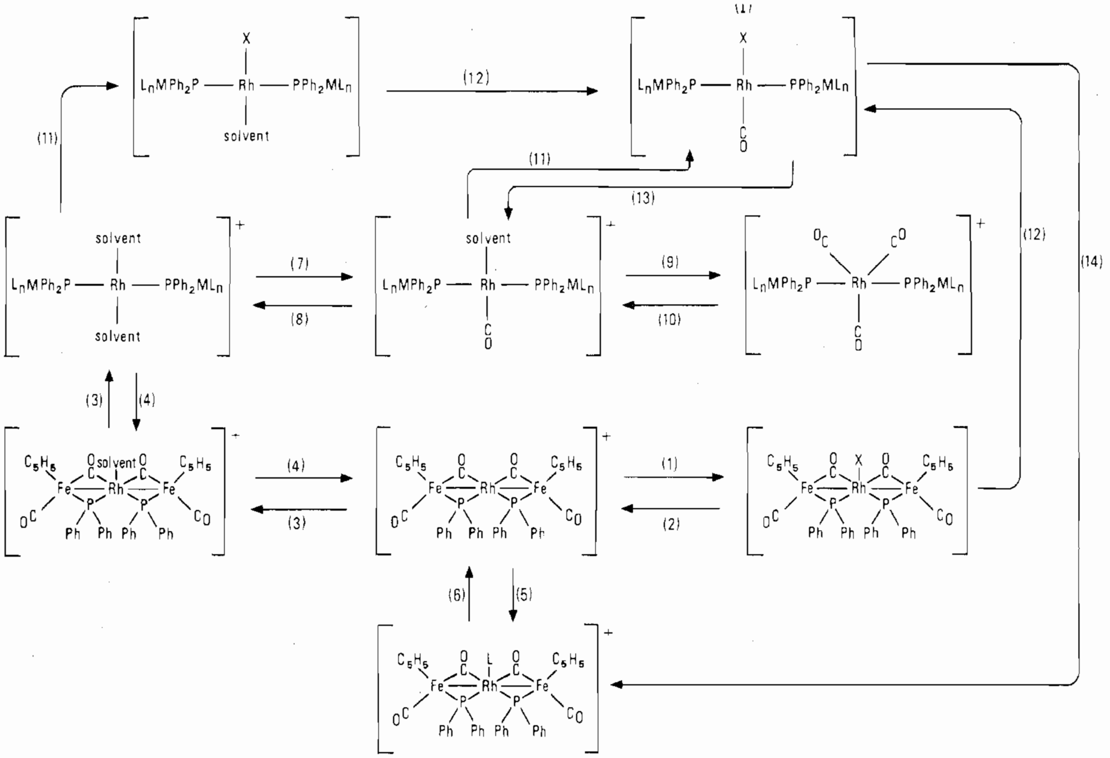
(43) P. J. Hendra and D. B. Powell, *Spectrochim. Acta*, **17**, 913 (1961).

(44) The C–O stretching frequencies for $[Rh\{P(C_6H_5)_2ML_n\}_2(\text{solvent})_x]^+$ are very similar to those for $[Rh(CO)\{P(C_6H_5)_2ML_n\}_2Cl]$ in solution (see Table I), which suggests that the infrared measurements on the solvento species might have in fact been made on the "carbonyl halide", produced by attack of the sodium chloride windows of the infrared cell on the solvento species (see text). To establish whether this was the case or not, we allowed an acetone solution of $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2]^+$ (II: $M' = Rh$; $R = H$) to stand in the infrared cell until the formation of $[Rh\{P(C_6H_5)_2ML_n\}_2(\text{acetone})_x]^+$ was complete. The cell contents were evaporated to dryness and the residue was extracted with carbon tetrachloride. No carbonyl-containing compound could be detected in the resultant CCl_4 solution by means of infrared spectroscopy. On the other hand extraction of the residue with CH_2Cl_2 afforded a solution which gave C–O stretching peaks corresponding to those for $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2]^+$ (II: $M' = Rh$; $R = H$).

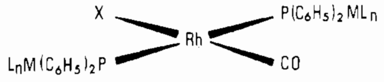
(45) These tests were essentially the same as those described above[44] except that the diglyme solutions were transferred from the cell when the peak at ca. 1800 cm^{-1} had reached maximum intensity. Furthermore because of the weak nature of this peak the procedure was repeated another five times and the six samples were combined. The residue isolated from the combined sample was extracted with an absolute minimum of carbon tetrachloride but even under these conditions neither $[Rh(CO)\{P(C_6H_5)_2ML_n\}_2Cl]$ (I) nor $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2Cl]$ could be detected in the CCl_4 extract.

Scheme I[a]



[a] (1) X^- in CH_2Cl_2. (2) Suitable counterion in ethanol. (3) Weakly coordinating solvent. (4) Loss of solvent. (5) $L = P(OCH_3)_3$ or $P(C_6H_5)_3$ in CH_2Cl_2. (6) Loss of L. (7) CO. (8) Weakly coordinating solvent. (9) CO in CH_2Cl_2. (10) Weakly coordinating solvent or heat in CH_2Cl_2. (11) X^-. (12) CO. (13) Ag^+ in weakly coordinating solvent. (14) $L = P(OCH_3)_3$ in CH_2Cl_2.

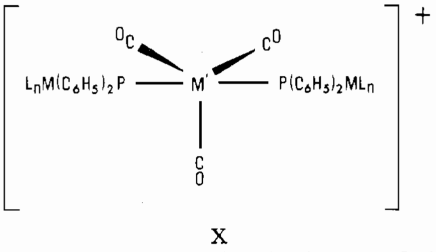
in the formation of $[Rh(CO)\{P(C_6H_5)_2ML_n\}_2Cl]$ (I: M′ = Rh; R = H) from either $[\{Rh(C_8H_{12})Cl\}_2]$ and $[P(C_6H_5)_2ML_n]$ or $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2]^+$ (II: M′ = Rh; R = H) and Cl^-, as well as being an intermediate in the formation of $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2]^+$ (II: M′ = Rh, R = H) from $[\{Rh(C_8H_{12})Cl\}_2]$ and $[P(C_6H_5)_2ML_n]$, is consistent with it being a 1:1 addition product of $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2]^+$ (II: M′ = Rh; R = H), viz., $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2Cl]$. Furthermore the presence of a single terminal and a single bridging carbonyl stretching peak in its IR spectrum is indicative of it having a structure similar to the latter but with the two bridging carbonyls essentially coplanar. Treatment of $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2]^+$ (II: M′ = Rh; R = H) with bromide, iodide, or cyanide ions also produced species containing bridging carbonyl groups, but these compounds converted too rapidly to $[Rh(CO)\{P(C_6H_5)_2ML_n\}_2X]$ (IX: X = Br, I, CN) to allow for their isolation from solution. The latter were sufficiently stable to isolate in pure form, however, and could be characterized fully. $[Ir\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2]^+$ (II: M′ = Ir; R = H) was also found to react very readily with halide ions, but while $[Ir\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2I]$ could be detected as an intermediate in the formation of $[Ir(CO)\{P(C_6H_5)_2ML_n\}_2I]$ (I: M′ = Ir; R = H), the halide and pseudohalide ion attack in the corresponding reactions involving chloride, bromide, and cyanide ions was too rapid for the detection of intermediate products.



IX

The bridged species $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_4R)\}_2]^+$ (II: M′ = Rh; R = H, CH_3) was readily regenerated from $[Rh(CO)\{P(C_6H_5)_2ML_n\}_2Cl]$ (I: M′ = Rh; R = H, CH_3), via the pathway outlined in Scheme I, by addition of silver ions to the latter in weakly coordinating solvents such as acetone, diglyme, or tetrahydrofuran. Intermediates, presumably $[Rh(CO)\{P(C_6H_5)_2ML_n\}_2(\text{solvent})_x]^+$ (solvent = acetone or THF) (cf. $[Rh(CO)\{P(C_6H_5)_3\}_2(\text{solvent})]^{+\,37}$), were detected in the reactions employing acetone and THF (e.g., ν(C–O) = 2032 (s) and 1983 (s) cm^{-1}, measured in acetone). Obviously because of the susceptibility of $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2]^+$ (II: M′ = Rh; R = H) to solvent attack, the total removal of the solvent was necessary for complete formation of the bridged product. Treatment of $[Ir(CO)\{P(C_6H_5)_2ML_n\}_2Cl]$ (I: M′ = Ir; R = H) with Ag^+ in THF similarly afforded $[Ir\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2]^+$ (II: M′ = Ir; R = H).

Passage of carbon monoxide through a dichloromethane or chloroform solution of $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2][A]$ (II[A]: M′ = Rh; R = H; A = $B(C_6H_5)_4$, SbF_6) led to the formation of a yellow crystalline product characterized as $[Rh(CO)_3\{P(C_6H_5)_2ML_n\}_2][A]$ (X[A]: M′ = Rh); elemental analysis could not readily distinguish between $[Rh(CO)_3\{P(C_6H_5)_2ML_n\}_2][A]$ and $[Rh(CO)_2\{P(C_6H_5)_2ML_n\}_2][A]$ and the compound was assumed to be the former on the basis that $[Rh(CO)_x\{P(C_6H_5)_3\}_2]^+$ and $[Ir(CO)_x\{P(C_6H_5)_3\}_2]^+$ occur as the tri- and not the dicarbonyl.[37,46] Significantly this carbonylation is reversible and refluxing of a solution of [Rh-



X

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(46) M. J. Church, M. J. Mays, R. N. F. Simpson, and F. P. Stefanini, *J. Chem. Soc. A*, 2909 (1970).

Table II. ^1H Nuclear Magnetic Resonance Spectroscopic Data

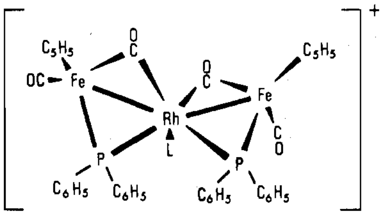
compd	proton resonances[a]		
	C_5H_5	C_6H_5	other
$[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2][PF_6]$[b]	5.17 s	7.28 m	
$[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2][B(C_6H_5)_4]$[b]	5.00 s	7.20 m 6.85 m	
$[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_4CH_3)\}_2][PF_6]$[c]	4.60 s 5.22 s	7.32 m	CH_3: 2.34 s
$[Ir\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2][SbF_6]$[d]	5.48 s	7.40 m	
$[Ir\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2][B(C_6H_5)_4]$[b]	5.02 s	7.20 m 6.84 m	
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3S(C_2H_5)][B(C_6H_5)_4]$[c]	4.92 s	7.22 m	CH_3: 1.17 t[e]
$[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2\{P(OCH_3)_3\}][B(C_6H_5)_4]$[b]	5.02 t[f] 4.85 t[h]	7.20 m	CH_3: 3.27 d[g]
$[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2(CO)_3][PF_6]$[b]	4.83 s	7.43 m	
$[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2(CO)_3][B(C_6H_5)_4]$[d]	5.10 s	7.30 m	
$[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2(CO)Cl]$[b]	5.15 s	7.25 m	
$[Ir\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2COCl]$[b]	5.16 s	7.26 m	

[a] δ scale in ppm relative to Me_4Si. Abbreviations: s, singlet; t, triplet; m, multiplet. [b] Measured in CD_2Cl_2. [c] Measured in $CDCl_3$. [d] Measured in CD_3COCD_3. [e] $J(PH) = 8.0$ Hz. [f] $J(PH) = 1.5$ Hz. [g] $J(PH) = 11.0$ Hz. [h] $J(PH) = 2.2$ Hz.

$(CO)_3\{P(C_6H_5)_2ML_n\}_2]^+$ (X: M′ = Rh) in CH_2Cl_2 gave $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2]^+$ (II: M′ = Rh; R = H) in virtually quantitative yield. Similar to that established for $[Rh(CO)_3\{P(C_6H_5)_3\}_2]^+$, $[Rh(CO)_3\{P(C_6H_5)_2ML_n\}_2]^+$ was found to lose carbon monoxide on dissolution in acetone, but the C–O stretching frequencies of the final product (ν(C–O) = 2022 (s), 1974 (s), and 1960 (ip) cm^{-1}, measured in acetone) were consistent with the formation of $[Rh\{P(C_6H_5)_2ML_n\}_2(\text{actone})_x]^+$ and not a monocarbonyl derivative as observed for $[Rh(CO)_3\{P(C_6H_5)_3\}_2]^+$.[37] The dichloromethane and tetrahydrofuran IR spectra of $[Rh(CO)_3\{P(C_6H_5)_2ML_n\}_2]^+$ (X: M′ = Rh) in the C–O stretching region are fairly similar to that of the solid-state spectrum, suggesting that the tricarbonyl structure is retained in these solvents. However, the possibility of the dicarbonyl product $[Rh(CO)_2\{P(C_6H_5)_2ML_n\}_2]^+$ being formed cannot be discounted.

The iridium species $[Ir\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2]^+$ (II: M′ = Ir; R = H) was also found to react very readily with carbon monoxide in $CHCl_3$ or CH_2Cl_2 but in this case a crystalline product could not be obtained for either the tetraphenylborate or the hexafluoroantimonate salt. Furthermore, the reaction proved to be irreversible while the C–O stretching peaks in the solid-state and dichloromethane IR spectra of the compound isolated from the reaction mixture gave band patterns significantly different to those for the same peaks in the corresponding spectra of $[Rh(CO)_3\{P(C_6H_5)_2ML_n\}_2]^+$ (X: M′ = Rh). Nevertheless in view of the ready formation of $[Ir(CO)_3\{P(C_6H_5)_3\}_2]^+$ from $[Ir(CO)\{P(C_6H_5)_3\}_2Cl]$ by passage of CO through an acetone solution of the latter,[46] the product is assumed to be $[Ir(CO)_3\{P(C_6H_5)_2ML_n\}_2]^+$ with the differences in the IR spectra being explained in terms of the two cations adopting different conformations.

The reaction of $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2][B(C_6H_5)_4]$ (II$[B(C_6H_5)_4]$: M′ = Rh; R = H) with an equimolar amount of $P(OCH_3)_3$ in CH_2Cl_2 under reflux for a short period did not effect a rearrangement of the molecular framework of the parent compound but afforded a 1:1 addition product of the latter, viz., $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2\{P(OCH_3)_3\}][B(C_6H_5)_4]$. The IR spectrum of this compound revealed three C–O stretching modes (one terminal and two bridging) whose relative frequencies were lower than the corresponding peaks of the parent (ν(C–O) = 1997 (s), 1823 (ms), and 1796 (m) cm^{-1}, measured in CH_2Cl_2; 1987 (s), 1812 (ms), and 1788 (m) cm^{-1}, measured as a Nujol mull). The proton NMR spectrum of the compound exhibited phenyl, cyclopentadienyl, and methyl resonances of the correct intensity ratio for the above formulation but, significantly, while a single doublet was observed in the methyl region two separate resonances of equal intensity were found in the cyclopentadienyl region. These spectroscopic results are interpreted in terms of the cation adopting a similar structure to its parent, XI, but with the trimethyl phosphite ligand not lying along



XI

the C_2 axis of II. $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2\{P(OCH_3)_3\}][B(C_6H_5)_4]$ was also synthesized by reacting $[Rh(CO)\{P(C_6H_5)_2ML_n\}_2Cl]$ (I: M′ = Rh; R = H) with an equimolar amount of $P(OCH_3)_3$ in CH_2Cl_2 under reflux followed by the addition of $Na[B(C_6H_5)_4]$, but this method also produced $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2]^+$ (II: M′ = Rh; R = H) which could not be separated from the trimethyl phosphite derivative.

An addition product containing both bridging and terminal carbonyls was also formed in the reaction of $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2][B(C_6H_5)_4]$ (II$[B(C_6H_5)_4]$: M′ = Rh; R = H) with $P(C_6H_5)_3$ under conditions similar to those above, but it readily degraded in solution to $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2][B(C_6H_5)_4]$ (II$[B(C_6H_5)_4]$: M′ = Rh; R = H) and could not be isolated analytically pure. However, the elemental analyses of the impure derivative and the isolation of this species in impure form from the reaction of $[Rh(C_8H_{12})P(C_6H_5)_3Cl]$ with $[FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)]$ in ethanol in the presence of $Na[B(C_6H_5)_4]$ are indicative of it being a 1:1 adduct with structure similar to the trimethyl phosphite derivative.

The reactions of $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2]^+$ (II: M′ = Rh; R = H) with $(C_6H_5)_2PCH_2P(C_6H_5)_2$, $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$, and phenyl isocyanide were also studied but pure products could not be isolated from any of them.

While $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2]^+$ (II: M′ = Rh; R = H) was intert toward dihydrogen at atmospheric pressure, $[Ir\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2]^+$ (II: M′ = Ir; R = H) readily reacted with this gas in solution to afford a product free of bridging carbonyl groups. This dihydrogen attack was found to be reversible and, as also recently noted by Norton et al.,[47] passage of dinitrogen through a solution of this com-

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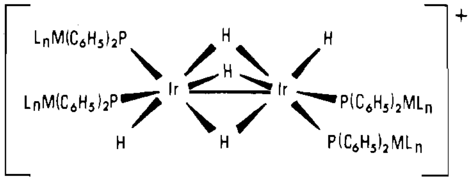
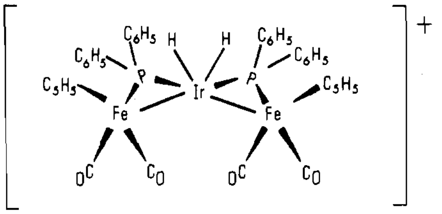
(47) A. Agapiou, R. F. Jordan, L. A. Zyzyck, and J. R. Norton, *J. Organomet. Chem.*, **141**, C35 (1977).

pound led to the regeneration of the parent compound. Attempts to isolate the hydride in crystalline form and pure enough for characterization proved unsuccessful, but the deep color of the compound suggested some form of metal–metal interaction occurring. It has recently been established that reaction of dihydrogen with $[Ir(C_8H_{12})\{P(C_6H_5)_3\}_2]^+$ in an inert solvent leads to the formation of dinuclear $[Ir_2(\mu\text{-}H)_3H_2\{P(C_6H_5)_3\}_2]^+$, the structure of which has been determined X-ray crystallographically.[48] A similar structure, XII, is possible



XII

for the hydride above. An alternative is that suggested by Norton et al., viz., XIII.[47] This structure is more consistent



XIII

with the NMR spectroscopic data obtained by the latter. $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2]^+$ (II: M′ = Rh; R = H) was found to react with H_2 at pressures of ca. 20 atm but the C–O stretching frequencies of the product were quite different to those of the corresponding iridium species and the reaction proved irreversible.

Summary

The study has shown that reaction of metal-containing ligands of the type DR_xML_n (D = donor atom, R = alkyl or aryl group, M = metal, L = ligand) with transition-metal derivatives provides a direct method for the synthesis of metal–metal bonded and possibly of clustered species, provided that the initial complex formed is coordinatively unsaturated or contains weakly bound ligands such that intramolecular rearrangement can readily occur.

This method has been employed to synthesize novel nonclosed species of the type $[M'\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_4R)\}_2]^+$ (II: M′ = Rh, Ir; R = H, CH_3) which, as well as having highly unusual molecular structures, react reversibly with carbon monoxide, dihydrogen, and weakly coordinating solvents such as acetone, tetrahydrofuran, diglyme, methanol, and acetonitrile.

Experimental Section

$[\{Rh(C_8H_{12})Cl\}_2]$,[32] $[\{Rh(CO)_2Cl\}_2]$,[49] $[\{Rh\{P(OC_6H_5)_3\}_2Cl\}_2]$,[36] $[Rh(C_8H_{12})P(C_6H_5)_3Cl]$,[32] $[\{Ir(C_8H_{12})Cl\}_2]$,[50] $[Fe(\eta\text{-}C_5H_5)(CO)_2Cl]$,[51] and $[Fe(\eta\text{-}C_5H_5)(CO)_2I]$[52] were synthesized according to literature methods. The mono- and bis(tertiary phosphines and phosphites), ethyl, *tert*-butyl, and phenyl mercaptan, $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2]$, and $[\{Fe(\eta\text{-}C_5H_4CH_3)(CO)_2\}_2]$ were obtained commercially. All experiments were performed under a dinitrogen atmosphere.

The IR spectra were recorded on Perkin-Elmer Model 21 and 457 instruments while the NMR spectra were obtained by using Varian Associates HA100 and T-60 spectrometers. Conductivity measurements were made on a Metrohm E365B instrument in $(1–10) \times 10^{-4}$ M acetone solutions. The elemental analyses were obtained by the Microanalytical Section of the National Chemical Research Laboratory, C.S.I.R., Pretoria, and the Alfred Bernhardt Microanalytical Laboratory, Elbach-über-Engelskirchen, West Germany.

(1) Synthesis of $[FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_4R)]$ (R = H or CH_3). Method 1. Excess lithium (ca. 1 g) was added to a solution of $P(C_6H_5)_3$ (1.0 g, 3.8 mmol) in THF (ca. 80 mL) and the solution stirred at room temperature for 24 h. The unreacted lithium was removed and a THF solution (ca. 10 mL) of $t\text{-}C_4H_9Cl$ (0.35 g, 3.8 mmol) added. The resultant solution was added dropwise to a solution of $[Fe(\eta\text{-}C_5H_5)(CO)_2Cl]$ (0.8 g, 3.8 mmol) or $[Fe(\eta\text{-}C_5H_5)(CO)_2I]$ (1.15 g, 3.8 mmol) in THF (ca. 30 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature and the THF removed under reduced pressure. The red residue was dissolved in benzene, the solution filtered, and the benzene removed under reduced pressure to afford $[FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)]$ as a dark red oil: yield 50% utilizing $[Fe(\eta\text{-}C_5H_5)(CO)_2Cl]$ as starting compound; 60% utilizing $[Fe(\eta\text{-}C_5H_5)(CO)_2I]$ as starting compound.

$[FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_4CH_3)]$ was prepared analogously from $[Fe(\eta\text{-}C_5H_4CH_3)(CO)_2X]$ (X = Cl, I).

Method 2. Excess sodium (ca. 0.5 g) was added to a THF solution (ca. 80 mL) of $P(C_6H_5)_2Cl$ (0.85 g, 3.8 mmol) and the solution stirred at room temperature for 12 h. The unreacted sodium was removed and the solution added dropwise to a solution of $[Fe(\eta\text{-}C_5H_5)(CO)_2Cl]$ (0.8 g, 3.8 mmol) or $[Fe(\eta\text{-}C_5H_5)(CO)_2I]$ (1.15 g, 3.8 mmol) in THF (ca. 30 mL) at −78 °C. $[FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)]$ was isolated from this solution as described in method 1: yield 60% utilizing $[Fe(\eta\text{-}C_5H_5)(CO)_2Cl]$ as starting material; 70% utilizing $[Fe(\eta\text{-}C_5H_5)(CO)_2I]$ as starting material.

Method 3. A THF solution (ca. 80 mL) of $Na[Fe(\eta\text{-}C_5H_5)(CO)_2]$, prepared by the method of Piper and Wilkinson from $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2]$ (0.8 g, 2.25 mmol) and 1% Na/Hg,[53] was added dropwise to a solution of $P(C_6H_5)_2Cl$ (1.0 g, 4.5 mmol) in THF (ca. 30 mL) at −78 °C and the reaction mixture allowed to warm slowly to room temperature. $[FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)]$ was isolated from the solution as described in method 1; yield 30%.

Method 4. A solution of $[Fe(\eta\text{-}C_5H_5)(CO)_2Cl]$ (1.0 g, 4.7 mmol) and $P(C_6H_5)_2H$ (0.9 g, 4.8 mmol) in acetone (ca. 60 mL) was stirred for 5 min. $Na[B(C_6H_5)_4]$ (1.65 g, 4.8 mmol) in methanol (ca. 5 mL) was added and the solvent removed under reduced pressure. The residue was washed with benzene and dissolved in acetone and the solution filtered. $[Fe(\eta\text{-}C_5H_5)(CO)_2\{P(C_6H_5)_2H\}][B(C_6H_5)_4]$ was isolated from this solution by addition of petroleum ether; yield 60%.

$[N(C_2H_5)_2H]$ (1.5 g, 20 mmol) in acetone (ca. 20 mL) was added to a solution of $[Fe(\eta\text{-}C_5H_5)(CO)_2\{P(C_6H_5)_2H\}][B(C_6H_5)_4]$ (1.0 g, 1.5 mmol) in acetone (ca. 30 mL). The solution was stirred for 30 min and the solvent removed under reduced pressure. The red residue was dissolved in benzene, and the solution filtered and evaporated to dryness to afford $[FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)]$ as a dark red oil, yield 50%.

(2) Syntheses of $[FeSR'(CO)_2(\eta\text{-}C_5H_5)]$ (R′ = C_2H_5, $t\text{-}C_4H_9$, C_6H_5). $[FeSR'(CO)_2(\eta\text{-}C_5H_5)]$ (R′ = C_2H_5, $t\text{-}C_4H_9$, C_6H_5) were prepared from NaSR′ and $[Fe(\eta\text{-}C_5H_5)(CO)_2Cl]$ by the method described by Knox et al.[54]

(3) Synthesis of $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}(C_8H_{12})][SbF_6]$. A solution of $Ag[SbF_6]$ (1.55 g, 1.6 mmol) in ethanol (ca. 20 mL) was added to a stirred suspension of $[\{Rh(C_8H_{12})Cl\}_2]$ (0.4 g, 0.8 mmol) in ethanol (ca. 20 mL). The AgCl which precipitated was separated by filtration, the light yellow filtrate cooled to −78 °C, and a solution of $[FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)]$ (0.65 g, 1.8 mmol) in ethanol (ca. 40 mL) added dropwise. The solution was kept at this temperature for a further 15 min and then at 0 °C for 24 h. The red precipitate of $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}(C_8H_{12})][SbF_6]$ which separated from the solution was collected by filtration, washed with cold ethanol (−78 °C) and petroleum ether, and dried in vacuo: yield 40%; conductivity 122 Ω^{-1} cm^2 mol^{-1}; color red. Anal. Calcd for $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}(C_8H_{12})][SbF_6]$: C, 40.1; H, 3.4; P, 3.8; Fe, 6.9; F, 14.1. Found: C, 40.3; H, 3.6; P, 4.0; Fe, 6.9; F, 13.8.

(4) Synthesis of $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}\{P(CH_3)_2C_6H_5\}_2][SbF_6]$. A solution of $Ag[SbF_6]$ (0.27 g, 0.8 mmol) in ethanol (ca. 20 mL) was added dropwise to a solution of $[\{Rh(C_8$-

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$H_{12})Cl\}_2]$ (0.2 g, 0.4 mmol) in ethanol (ca. 20 mL) and the AgCl which precipitated separated by filtration. A solution of $P(CH_3)_2C_6H_5$ (0.22 g, 1.6 mmol) in ethanol (ca. 20 mL) was added dropwise to this solution. Addition of petroleum ether to the resultant solution afforded yellow crystals of $[Rh(C_8H_{12})\{P(CH_3)_2C_6H_5\}_2][SbF_6]$ which were further purified by recrystallization from acetone/petroleum ether: yield 40%; conductivity 142 Ω^{-1} cm^{-2} mol^{-1}; color yellow. Anal. Calcd for $[Rh(C_8H_{12})\{P(CH_3)_2C_6H_5\}_2][SbF_6]$: C, 39.9; H, 4.7; P, 8.6. Found: C, 39.8; H, 4.8; P, 8.6.

An ethanol solution (ca. 20 mL) of $[FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)]$ (0.4 g, 1.1 mmol) was added dropwise to a stirred suspension of $[Rh(C_8H_{12})\{P(CH_3)_2C_6H_5\}_2][SbF_6]$ (0.65 g, 0.90 mmol) in ethanol (ca. 20 mL). The reaction mixture was refluxed very briefly and then kept at 0 °C for 24 h. The red precipitate of $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}\{P(CH_3)_2C_6H_5\}_2][SbF_6]$ which formed was separated from the mother liquor by decantation, washed with cold ethanol (−78 °C) and petroleum ether, and dried in vacuo: yield 40%; conductivity 120 Ω^{-1} cm^2 mol^{-1}; color red. Anal. Calcd for $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}\{P(CH_3)_2C_6H_5\}_2][SbF_6]$: C, 43.0; H, 3.8; P, 9.5; Fe, 11.7. Found: C, 43.2; H, 4.0; P, 9.2; Fe, 11.5.

(5) Synthesis of $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}\{P(OC_6H_5)_3\}_2][SbF_6]$. A solution of $[FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)]$ (0.55 g, 1.5 mmol) was added dropwise to a stirred ethanol solution (ca. 20 mL) of $[Rh\{P(OC_6H_5)_3\}_2(ethanol)_x][SbF_6]$ at −78 °C; the latter was prepared in situ from $[\{Rh\{P(OC_6H_5)_3\}_2Cl\}_2]$ (1.0 g, 0.66 mmol) and $Ag[SbF_6]$ (0.48 g, 1.4 mmol) in ethanol by the method adopted for the synthesis of $[Rh(C_8H_{12})(ethanol)_x][SbF_6]$ described in (3). The solution was stirred at this temperature for 3 h and then kept at 0 °C for 12 h. $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}\{P(OC_6H_5)_3\}_2][SbF_6]$ which separated as a red solid was isolated and purified as described in (3): yield 60%; conductivity 140 Ω^{-1} cm^2 mol^{-1}; color red. Anal. Calcd for $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}\{P(OC_6H_5)_3\}_2][SbF_6]$: C, 50.0; H, 3.4; P, 7.0; Fe, 4.2; F, 8.6. Found: C, 49.9; H, 3.6; P, 7.0; Fe, 4.1; F, 8.6.

(6) Synthesis of $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}(C_6H_5)_2PC_2H_4P(C_6H_5)_2][SbF_6]$. $[Rh(C_8H_{12})(C_6H_5)_2PC_2H_4P(C_6H_5)_2][SbF_6]$ was synthesized from $[\{Rh(C_8H_{12})Cl\}_2]$ (0.2 g, 0.4 mmol) and $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ (0.32 g, 0.8 mmol) by the method described for the preparation of $[Rh(C_8H_{12})\{P(CH_3)_2C_6H_5\}_2][SbF_6]$ in (4): yield 50%; conductivity 110 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $[Rh(C_8H_{12})(C_6H_5)_2PC_2H_4P(C_6H_5)_2][SbF_6]$: C, 48.3; H, 4.3; P, 7.3. Found: C, 48.5; H, 4.4; P, 7.2.

$[FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)]$ (0.36 g, 1.0 mmol) in ethanol (ca. 30 mL) was added dropwise to a stirred suspension of $[Rh(C_8H_{12})(C_6H_5)_2PC_2H_4P(C_6H_5)_2][SbF_6]$ (0.67 g, 0.8 mmol) in ethanol (ca. 20 mL) as described in (4) to give $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}(C_6H_5)_2PC_2H_4P(C_6H_5)_2][SbF_6]$ which was isolated and purified as described for $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}\{P(CH_3)_2C_6H_5\}_2][SbF_6]$: yield 30%; conductivity 115 Ω^{-1} cm^2 mol^{-1}; color red. Anal. Calcd for $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}(C_6H_5)_2PC_2H_4P(C_6H_5)_2][SbF_6]$: C, 49.2; H, 3.6; P, 8.5. Found: C, 49.3; H, 3.8; P, 8.6.

(7) Synthesis of $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_4R)\}_2][A]$ (R = H, CH_3; A = SbF_6, PF_6, $B(C_6H_5)_4$). Method 1. An ethanol solution (ca. 40 mL) of $[FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)]$ (1.1 g, 3.0 mmol) was added dropwise to a suspension of $[\{Rh(C_8H_{12})Cl\}_2]$ (0.3 g, 0.6 mmol) in ethanol (ca. 15 mL) at −78 °C. On dissolution of all of the $[\{Rh(C_8H_{12})Cl\}_2]$, a solution of $Na[B(C_6H_5)_4]$ (0.4 g, 1.3 mmol) or $[NH_4][PF_6]$ (0.21 g, 1.3 mmol) in ethanol (ca. 5 mL) was added with stirring. The red precipitate of $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2][A]$ which separated from solution was isolated by filtration, washed with benzene, and purified further by crystallization from dichloromethane/petroleum ether: yield 70% for both salts; for A = PF_6 conductivity 139 Ω^{-1} cm^2 mol^{-1}, color red; for A = $B(C_6H_5)_4$ conductivity 91 Ω^{-1} cm^2 mol^{-1}, color red. Anal. Calcd for $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2][PF_6]$: C, 47.0; H, 3.1; P, 9.6; F, 11.7. Found: C, 47.5; H, 3.1; P, 9.4; F, 11.7. Anal. Calcd for $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2][B(C_6H_5)_4]$: C, 65.0; H, 4.4; P, 5.6; B, 0.8. Found: C, 65.2; H, 4.3; P, 5.2; B, 0.8.

$[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_4CH_3)\}_2][PF_6]$ was obtained analogously from $[\{Rh(C_8H_{12})Cl\}_2]$ and $[FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_4CH_3)]$: conductivity 139 Ω^{-1} cm^2 mol^{-1}; color red. Anal. Calcd for $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_4CH_3)\}_2][PF_6]$: C, 48.0; H, 3.4; P, 9.3; F, 11.4. Found: C, 47.8; H, 3.4; P, 9.3; F, 11.6.

Method 2. A solution of $Ag[SbF_6]$ (0.55 g, 1.6 mmol) in THF (ca. 20 mL) was added with stirring to a solution of $[\{Rh(C_8H_{12})Cl\}_2]$ (0.4 g, 0.8 mmol) in THF (ca. 20 mL). The AgCl which precipitated was separated by filtration, the light yellow filtrate cooled to −78 °C, and a solution of $[FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)]$ (1.45 g, 4.0 mmol) in THF (ca. 40 mL) added dropwise. The volume of the solution was reduced under vacuum and the $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2][SbF_6]$ crystallized by addition of petroleum ether: yield 70%; conductivity 140 Ω^{-1} cm^2 mol^{-1}; color red. Anal. Calcd. for $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2][SbF_6]$: C, 42.9; H, 2.9; P, 5.8; Fe, 10.5. Found: C, 43.0; H, 2.5; P, 5.6; Fe, 10.0.

(8) Synthesis of $[Ir\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2][A]$ (A = SbF_6, $B(C_6H_5)_4$). Method 1. A THF solution (ca. 40 mL) of $[Ir(C_8H_{12})(THF)_x][SbF_6]$ was synthesized from $[\{Ir(C_8H_{12})Cl\}_2]$ (0.27 g, 0.4 mmol) by addition of $Ag[SbF_6]$ (0.28 g, 0.81 mmol) in THF according to the method described for the synthesis of $[Rh(C_8H_{12})(THF)_x][SbF_6]$ in (7). A solution of $[FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)]$ (0.72 g, 2.0 mmol) in THF (ca. 40 mL) was added dropwise to this solution at −78 °C and the resultant reaction mixture kept at this temperature for 15 min. The solvent was quickly removed under reduced pressure and the dark red residue of $[Ir\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2][SbF_6]$ washed with benzene and crystallized from dichloromethane/petroleum ether: yield 20%; conductivity 127 Ω^{-1} cm^2 mol^{-1}; color rust red. Anal. Calcd for $[Ir\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2][SbF_6]$: C, 39.6; H, 2.6; P, 5.4; Fe, 10.0. Found: C, 39.1; H, 2.9; P, 5.3; Fe, 9.8.

Method 2. An ethanol solution (ca. 30 mL) of $[FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)]$ (1.09 g, 3 mmol) was added dropwise to a solution of $[Ir(C_8H_{12})(ethanol)_x][BF_4]$ in ethanol (ca. 20 mL) at −78 °C, the latter being prepared in situ from $[\{Ir(C_8H_{12})Cl\}_2]$ (0.4 g, 0.6 mmol) and $Ag[BF_4]$ (0.23 g, 1.2 mmol). The resultant solution was stirred for a further 15 min at this temperature and a solution of $Na[B(C_6H_5)_4]$ (0.4 g, 1.3 mmol) in ethanol (ca. 8 mL) added. The reaction mixture was allowed to warm to room temperature and the red precipitate which separated isolated by means of filtration. Crystallization from dichloromethane/chloroform/petroleum ether afforded $[Ir\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2][B(C_6H_5)_4]$ as rust red crystals: yield 70%; conductivity 83 Ω^{-1} cm^2 mol^{-1}; color rust red. Anal. Calcd for $[Ir\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2][B(C_6H_5)_4]$: C, 60.3; H, 4.1. Found: C, 59.3; H, 3.9.

(9) Synthesis of $[Rh\{FeS(t\text{-}C_4H_9)(CO)_2(\eta\text{-}C_5H_5)\}_2][A]$ (A = SbF_6, $B(C_6H_5)_4$). Method 1. An ethanol solution (ca. 20 mL) of $Ag[SbF_6]$ (0.79 g, 2.3 mmol) was added dropwise to a stirred suspension of $[\{Rh(C_8H_{12})Cl\}_2]$ (0.57 g, 1.15 mmol) in ethanol (ca. 20 mL). The AgCl which precipitated was separated by filtration, the light yellow filtrate cooled to −78 °C, and a solution of $[FeS(t\text{-}C_4H_9)(CO)_2(\eta\text{-}C_5H_5)]$ (1.53 g, 5.75 mmol) in ethanol (ca. 40 mL) added dropwise. The solution was allowed to warm to room temperature and left at this temperature for 2 h before being kept at 0 °C for 24 h. The green precipitate of $[Rh\{FeS(t\text{-}C_4H_9)(CO)_2(\eta\text{-}C_5H_5)\}_2][SbF_6]$ which separated was isolated, washed with cold ethanol (−78 °C) and further purified by crystallization from dichloromethane/petroleum ether: yield 40%; conductivity 142 Ω^{-1} cm^2 mol^{-1}; color green. Anal. Calcd for $[Rh\{FeS(t\text{-}C_4H_9)(CO)_2(\eta\text{-}C_5H_5)\}_2][SbF_6]$: C, 30.3; H, 3.2; S, 7.4. Found: C, 30.1; H, 3.2; S, 7.3.

Method 2. A solution of $[FeS(t\text{-}C_4H_9)(CO)_2(\eta\text{-}C_5H_5)]$ (0.53 g, 2.0 mmol) in methanol (ca. 20 mL) was added dropwise to a stirred suspension of $[\{Rh(C_8H_{12})Cl\}_2]$ (0.2 g, 0.4 mmol) in methanol (ca. 20 mL) at −78 °C. The solution was allowed to warm slowly to 0 °C and a solution of $Na[B(C_6H_5)_4]$ (0.58 g, 1.7 mmol) in methanol (ca. 5 mL) added. The solvent was removed under reduced pressure and the residue washed with benzene. Green crystals of $[Rh\{FeS(t\text{-}C_4H_9)(CO)_2(\eta\text{-}C_5H_5)\}_2][B(C_6H_5)_4]$ were obtained by crystallization of the residue from dichloromethane/ethanol/petroleum ether; yield 15%. The compound was identified by means of IR spectroscopy only.

(10) Formation of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3S(t\text{-}C_4H_9)][B(C_6H_5)_4]$ in the Attempted Synthesis of $[Rh\{FeS(t\text{-}C_4H_9)(CO)_2(\eta\text{-}C_5H_5)\}_2][B(C_6H_5)_4]$. A methanol solution (ca. 20 mL) of $[FeS(t\text{-}C_4H_9)(CO)_2(\eta\text{-}C_5H_5)]$ (0.65 g, 2.4 mmol) was added dropwise to a stirred suspension of $[\{Rh(C_8H_{12})Cl\}_2]$ (0.2 g, 0.4 mmol) in methanol (ca. 20 mL). A methanol solution (ca. 5 mL) of $Na[B(C_6H_5)_4]$ (0.27 g, 0.8 mmol) was added to this solution and the solution was stirred for a further hour. The reaction mixture was evaporated to dryness and the residue washed with benzene and dissolved in acetone and the solution filtered. Addition of methanol and petroleum ether to the filtrate gave $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3S(t\text{-}C_4H_9)][B(C_6H_5)_4]$ as olive green crystals: yield 10%; conductivity 100 Ω^{-1} cm^2 mol^{-1}; color olive green. Anal. Calcd for $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3S(t\text{-}C_4H_9)][B(C_6H_5)_4]$: C, 67.1;

H, 5.4; S, 4.4. Found: C, 66.4; H, 5.4; S, 4.6.

(11) Formation of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3S(C_2H_5)][B(C_6H_5)_4]$ in the Attempted Synthesis of $[Rh\{FeS(C_2H_5)(CO)_2(\eta\text{-}C_5H_5)\}_2][B(C_6H_5)_4]$. A methanol solution (ca. 20 mL) of $[FeS(C_2H_5)(CO)_2(\eta\text{-}C_5H_5)]$ (0.5 g, 2.1 mmol) was added dropwise to a stirred suspension of $[\{Rh(C_8H_{12})Cl\}_2]$ (0.2 g, 0.4 mmol) in ethanol (ca. 20 mL) at −78 °C. The solution was stirred for a further hour at this temperature and a solution of $Na[B(C_6H_5)_4]$ (0.27 g, 0.8 mmol) in methanol (ca. 5 mL) added. The resultant precipitate was rapidly separated from the mother liquor and washed with cold methanol (−78 °C), petroleum ether, benzene, and petroleum ether. The olive green residue of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3S(C_2H_5)][B(C_6H_5)_4]$ was crystallized from dichloromethane/petroleum ether: yield 40%; conductivity 103 Ω^{-1} cm^2 mol^{-1}; color olive green. Anal. Calcd for $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3S(C_2H_5)][B(C_6H_5)_4]$: C, 65.7; H, 5.1; S, 4.6. Found: C, 65.7; H, 5.1; S, 4.5.

(12) Synthesis of $[Rh\{FeS(C_6H_5)(CO)_2(\eta\text{-}C_5H_5)\}_2(C_8H_{12})][SbF_6]$. A solution of $Ag[SbF_6]$ (0.56 g, 1.6 mmol) in ethanol (ca. 20 mL) was added dropwise to a stirred suspension of $[\{Rh(C_8H_{12})Cl\}_2]$ (0.4 g, 0.8 mmol) in ethanol (ca. 20 mL). The AgCl which precipitated was separated by filtration, the light yellow filtrate cooled to −78 °C, and a solution of $[FeS(C_6H_5)(CO)_2(\eta\text{-}C_5H_5)]$ (1.0 g, 3.5 mmol) in ethanol (ca. 40 mL) added dropwise. The solution was allowed to warm to room temperature and kept at 0 °C for 24 h. The resultant orange precipitate was separated from the mother liquor, washed with cold ethanol (−78 °C), and dried in vacuo: yield 80%; conductivity 116 Ω^{-1} cm^2 mol^{-1}; color orange. Anal. Calcd for $[Rh\{FeS(C_6H_5)(CO)_2(\eta\text{-}C_5H_5)\}_2(C_8H_{12})][SbF_6]$: C, 40.1; H, 3.2; S, 6.3. Found: C, 39.7; H, 3.2; S, 6.4.

(13) Synthesis of $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_4R)\}_2(CO)X]$ (R = H, CH$_3$; X = Cl, I, CN). Method 1. A solution of $[FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)]$ (0.91 g, 2.5 mmol) or $[FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_4CH_3)]$ (0.94 g, 2.5 mmol) in benzene (ca. 30 mL) was added dropwise to a solution of $[\{Rh(CO)_2Cl\}_2]$ (0.2 g, 0.52 mmol) in benzene (ca. 30 mL). The reaction mixture was allowed to stand for 1 h at room temperature and petroleum ether (ca. 10 mL) added. Storage of this solution at 0 °C for 24 h led to the separation of a microcrystalline precipitate of $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_4R)\}_2(CO)Cl]$ (R = H, CH$_3$) which was isolated by centrifugation, washed with petroleum ether, and dried in vacuo: yield $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2(CO)Cl]$ 70%; $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_4CH_3)\}_2(CO)Cl]$ 60%.

Method 2. $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2(CO)Cl]$ was synthesized from $[\{Rh(C_8H_{12})Cl\}_2]$ (0.2 g, 0.4 mmol) and $[FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)]$ (0.72 g, 2.0 mmol) in benzene following a procedure analogous to that described in method 1.

Method 3. An aqueous solution (ca. 10 mL) of $[N(C_2H_5)_4]Cl$ (0.6 g, 0.36 mmol) or KI (0.06 g, 0.36 mmol) or KCN (0.023 g, 0.35 mmol) was added dropwise to a stirred acetone solution (ca. 30 mL) of $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2(CO)_3][SbF_6]$ (0.37 g, 0.33 mmol). The reaction mixture was stirred for a further 20 min and then kept at 0 °C for 24 h. The resultant precipitate of $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2(CO)X]$ (X = Cl, I, CN) was separated from the mother liquor, washed with water, and dried in vacuo: yields 50–60%; for X = Cl and R = H conductivity 4.5 Ω^{-1} cm^2 mol^{-1}, color yellow; for X = Cl and R = CH$_3$ conductivity 1.7 Ω^{-1} cm^2 mol^{-1}, color yellow; for X = I and R = H conductivity 0.5 Ω^{-1} cm^2 mol^{-1}, color yellow; for X = CN and R = H conductivity 1.8 Ω^{-1} cm^2 mol^{-1}, color yellow. Anal. Calcd for $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2(CO)Cl]$: C, 52.6; H, 3.4; P, 7.0; Fe, 12.5; Cl, 4.0. Found: C, 52.2; H, 3.3; P, 6.8; Fe, 12.8; Cl, 4.2. Anal. Calcd for $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_4CH_3)\}_2(CO)Cl]$: C, 53.6; H, 3.7; P, 6.8; Cl, 3.9; Rh, 11.2; mol wt 919. Found: C, 53.4, H, 3.4; P, 6.8; Cl, 3.7; Rh, 11.4; mol wt 1035. Anal. Calcd for $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2(CO)I]$: C, 47.8; H, 3.2; P, 6.5; I, 13.3. Found: C, 47.9; H, 3.2; P, 6.5; I, 13.3. Anal. Calcd for $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2(CO)CN]$: C, 54.5; H, 3.4; P, 7.0; N, 1.6. Found: C, 54.0; H, 3.5; P, 7.0; N, 1.5.

(14) Synthesis of $[Ir\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_4R)\}_2(CO)Cl]$ (R = H, CH$_3$). Yellow microcrystals of $[Ir\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_4R)\}_2(CO)Cl]$ (R = H, CH$_3$) were obtained from $[\{Ir(C_8H_{12})Cl\}_2]$ (0.2 g, 0.3 mmol) and $[FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)]$ (0.54 g, 1.5 mmol) or $[FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_4CH_3)]$ (0.55 g, 1.5 mmol) in benzene by the method described for the synthesis of $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2(CO)Cl]$ from $[\{Rh(C_8H_{12})Cl\}_2]$ in (13): yields 30%; for R = H conductivity 4.0 Ω^{-1} cm^2 mol^{-1}, color yellow; for R = CH$_3$ conductivity 8.0 Ω^{-1} cm^2 mol^{-1}, color yellow. Anal. Calcd for $[Ir\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2(CO)Cl]$: C, 47.8; H, 3.1; Cl, 3.6. Found: C, 44.9; H, 3.2; Cl, 4.3. (Compound could not be obtained analytically pure.) Anal. Calcd for $[Ir\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_4CH_3)\}_2(CO)Cl]$: C, 48.9; H, 3.4; P, 6.2. Found: C, 48.5; H, 3.6; P, 5.9.

(15) Reaction of $[\{Rh(CO)_2Cl\}_2]$ with $[FeS(C_6H_5)(CO)_2(\eta\text{-}C_5H_5)]$. An ethanol solution (ca. 20 mL) of $[FeS(C_6H_5)(CO)_2(\eta\text{-}C_5H_5)]$ (0.51 g, 1.8 mmol) was added dropwise to a stirred solution of $[\{Rh(CO)_2Cl\}_2]$ (0.31 g, 0.8 mmol) in ethanol (ca. 20 mL). The reaction mixture was kept at 0 °C for 24 h during which time red crystals of $[\{Rh(CO)_2SC_6H_5\}_2]$ separated. These were isolated, washed with cold ethanol (−78 °C) and dried in vacuo: yield 70%; conductivity 1.2 Ω^{-1} cm^2 mol^{-1}; color red. Anal. Calcd for $[\{Rh(CO)_2SC_6H_5\}_2]$: C, 35.8; H, 1.9; S, 12.0; mol wt 536. Found: C, 35.7; H, 1.8; S, 11.8; mol wt 537.

The mother liquor was shown to contain $[Fe(\eta\text{-}C_5H_5)(CO)_2Cl]$ on the basis of IR spectroscopic evidence. Analogous results were obtained by using benzene as solvent.

(16) Reaction of $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2][SbF_6]$ with Cl$^-$, I$^-$, or CN$^-$. A solution of $[N(C_2H_5)_4]Cl$ (0.08 g, 0.49 mmol) in dichloromethane (ca. 30 mL) was added dropwise to a stirred dichloromethane solution (ca. 30 mL) of $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2][SbF_6]$ (0.5 g, 0.47 mmol). The solution was stirred at room temperature for 45 min, reduced to a volume of ca. 15 mL, and filtered. Petroleum ether was added to the filtrate to afford a green precipitate which was separated from the mother liquor, washed with petroleum ether, and dried in vacuo. The compound degraded to $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2(CO)Cl]$ on attempted crystallization and thus could not be obtained analytically pure. It was identified as $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2Cl]$ (see Results and Discussion) by means of IR spectroscopy (see Table I for ν(C–O)): conductivity 2 Ω^{-1} cm^2 mol^{-1}; color green.

Treatment of $[Rh\{FeP(C_6H_6)_2(CO)_2(\eta\text{-}C_5H_5)\}_2][SbF_6]$ with $[N(C_2H_5)_4]I$ or KCN in dichloromethane or acetone/water similarly afforded green solutions but these rapidly turned yellow due to the formation of $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2(CO)X]$. The green products were identified as $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2X]$ (X = I, CN) by means of IR spectroscopy (see Table I for ν(C–O)).

Because of the ready conversion of $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2X]$ to $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2(CO)X]$ (X = Cl, I, CN) the reaction of $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2]^+$ with X$^-$ in THF or acetone/water provided an alternative method for the synthesis of $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2(CO)X]$.

(17) Synthesis of $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2\{P(OCH_3)_3\}][B(C_6H_5)_4]$. A solution of $P(OCH_3)_3$ (0.08 g, 0.65 mmol) in dichloromethane (ca. 30 mL) was added dropwise to a dichloromethane solution (ca. 30 mL) of $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2][B(C_6H_5)_4]$ (0.5 g, 0.44 mmol) and the solution refluxed for 5 min. The solvent was removed under reduced pressure and the red residue of $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2\{P(OCH_3)_3\}][B(C_6H_5)_4]$ was washed with benzene and crystallized from dichloromethane/methanol: yield 25%; conductivity 84 Ω^{-1} cm^2 mol^{-1}; color red. Anal. Calcd for $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2\{P(OCH_3)_3\}][B(C_6H_5)_4]$: C, 61.5; H, 4.7; P, 7.3; Fe, 8.8; B, 0.9. Found: C, 62.2; H, 4.5; P, 7.2; Fe, 8.6; B, 0.7.

(18) Reaction of $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2][B(C_6H_5)_4]$ with $P(C_6H_5)_3$. A solution of $P(C_6H_5)_3$ (0.12 g, 0.46 mmol) in dichloromethane (ca. 20 mL) was added to a dichloromethane solution (ca. 30 mL) of $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2][B(C_6H_5)_4]$ and the reaction mixture refluxed for 5 min. The solvent was removed under reduced pressure to afford a red residue with C–O stretching frequencies at 2002 (s) and 1806 (ms) cm^{-1}, measured in CH_2Cl_2. Attempts to crystallize this residue led to its degradation to $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2][B(C_6H_5)_4]$. On the basis of the IR spectroscopic results the product of this reaction is proposed to be $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2\{P(C_6H_5)_3\}][B(C_6H_5)_4]$ (see Results and Discussion).

(19) Synthesis of $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_2)\}_2(CO)_3][A]$ (A = SbF$_6$, B(C$_6$H$_5$)$_4$). Carbon monoxide was bubbled through a suspension of $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2][A]$ (0.5 g) (A = SbF$_6$, B(C$_6$H$_5$)$_4$) in chloroform (ca. 15 mL). The complex immediately dissolved and the solution turned yellow. The passage of the carbon monoxide was continued until the volume of the soluton had been reduced to ca. 5 mL. The solution was filtered and yellow crystals of $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2(CO)_3][A]$ were obtained by addition of a little petroleum ether: yield 70%; for A = SbF$_6$ con-

Inorg. Chem. **1980**, *19*, 587–593

ductivity 90 Ω^{-1} cm^2 mol^{-1}, color yellow; for A = $B(C_6H_5)_4$ conductivity 82 Ω^{-1} cm^2 mol^{-1}, color yellow. Anal. Calcd for $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2(CO)_3][SbF_6]$: C, 42.9; H, 2.7; P, 5.5; Fe, 10.0; F, 10.2. Found: C, 42.9; H, 2.7; P, 5.5; Fe, 9.8; F, 10.3. Anal. Calcd for $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2(CO)_3][B(C_6H_5)_4]$: P, 5.2; Fe, 9.3; B, 0.9. Found: P, 5.2; Fe, 9.4; B, 1.0.

(20) Reaction of $[Ir\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2][B(C_6H_5)_4]$ with Carbon Monoxide. Carbon monoxide was bubbled through a chloroform suspension (ca. 10 mL) of $[Ir\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2][B(C_6H_5)_4]$ (0.5 g) until complete dissolution of this compound had been effected. The solvent was removed under reduced pressure to afford a yellow residue which was shown to contain $[Ir\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2(CO)_3][B(C_6H_5)_4]$ by means of IR spectroscopy; numerous attempts to obtain this compound analytically pure proved unsuccessful.

(21) Reaction of $[Ir\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2][B(C_6H_5)_4]$ with Dihydrogen. Dihydrogen was bubbled through a suspension of $[Ir\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2][B(C_6H_5)_4]$ (0.5 g) in chloroform (ca. 10 mL) for 15 min. An IR spectrum of the resultant solution revealed the absence of bridging carbonyl stretching peaks but attempts to isolate the product in crystalline form proved unsuccessful. Passage of dinitrogen through the solution led to the regeneration of $[Ir\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2][B(C_6H_5)_4]$ (see Results and Discussion for a discussion of this species).

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Registry No. $FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)$, 38816-40-9; $FeS(C_2H_5)(CO)_2(\eta\text{-}C_5H_5)$, 12108-34-8; $FeS(t\text{-}C_4H_9)(CO)_2(\eta\text{-}C_5H_5)$, 38816-45-4; $FeS(C_6H_5)(CO)_2(\eta\text{-}C_5H_5)$, 12110-44-0; $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}(C_8H_{12})][SbF_6]$, 72228-85-4; $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}\{P(CH_3)_2C_6H_5\}_2][SbF_6]$, 72228-87-6; $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}\{P(OC_6H_5)_3\}_2][SbF_6]$, 72268-98-5; $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}\{P(OC_6H_5)_3\}_2][SbF_6]$, 72268-98-5; $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}\{(C_6H_5)_2PC_2H_4P(C_6H_5)_2\}][SbF_6]$, 72228-89-8; $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2][PF_6]$, 37299-51-7; $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2][SbF_6]$, 37299-52-8; $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2][B(C_6H_5)_4]$, 37299-50-6; $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_4CH_3)\}_2][PF_6]$, 38903-34-3; $[Ir\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2][SbF_6]$, 37299-53-9; $[Ir\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2][B(C_6H_5)_4]$, 72137-99-6; $[Rh\{FeS(t\text{-}C_4H_9)(CO)_2(\eta\text{-}C_5H_5)\}_2][SbF_6]$, 37299-06-2; $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3S(C_2H_5)][B(C_6H_5)_4]$, 56953-82-3; $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3S(t\text{-}C_4H_9)][B(C_6H_5)_4]$, 56953-84-5; $[Rh\{FeS(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2(C_8H_{12})][SbF_6]$, 72138-01-3; $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2\{P(OCH_3)_3\}][B(C_6H_5)_4]$, 37299-55-1; $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2\{P(C_6H_5)_3\}][B(C_6H_5)_4]$, 37299-60-8; $[Rh(CO)_3\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2][PF_6]$, 72138-03-5; $[Rh(CO)_3\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2][SbF_6]$, 72173-26-3; $[Rh(CO)_3\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2][B(C_6H_5)_4]$, 72173-27-4; $[Ir(CO)_3\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2][B(C_6H_5)_4]$, 72243-71-1; $Rh(CO)\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2Cl$, 72252-31-4; $Rh(CO)\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_4CH_3)\}_2Cl$, 72252-32-5; $Ir(CO)\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2Cl$, 72138-09-1; $Ir(CO)\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_4CH_3)\}_2Cl$, 72138-10-4; $Rh(CO)\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2Br$, 72138-11-5; $Ir(CO)\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2Br$, 72138-12-6; $Rh(CO)\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2I$, 72138-13-7; $Rh(CO)\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_4CH_3)\}_2I$, 72152-02-4; $Ir(CO)\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2I$, 72138-14-8; $Rh(CO)\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2CN$, 72138-15-9; $Ir(CO)\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2CN$, 72138-16-0; $Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2Cl$, 72152-03-5; $Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2Br$, 72252-33-6; $Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2I$, 72138-17-1; $Ir\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2I$, 72138-18-2; $Rh\{FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_5)\}_2CN$, 72138-19-3; $[Rh\{FeS(t\text{-}C_4H_9)(CO)_2(\eta\text{-}C_5H_5)\}_2][B(C_6H_5)_4]$, 72138-20-6; $FeP(C_6H_5)_2(CO)_2(\eta\text{-}C_5H_4CH_3)$, 38816-41-0; $[Fe(\eta\text{-}C_5H_5)(CO)_2\{P(C_6H_5)_2H\}][B(C_6H_5)_4]$, 72138-21-7; $[Rh(C_8H_{12})\{P(CH_3)_2C_6H_5\}_2][SbF_6]$, 72138-23-9; $[Rh(C_8H_{12})(C_6H_5)_2PC_2H_4P(C_6H_5)_2][SbF_6]$, 72138-24-0; $Fe(\eta\text{-}C_5H_5)(CO)_2Cl$, 12107-04-9; $Fe(\eta\text{-}C_5H_5)(CO)_2I$, 12078-28-3; $\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2$, 12154-95-9; $\{Rh(C_8H_{12})Cl\}_2$, 12092-47-6; $\{Rh\{P(OC_6H_5)_3\}_2Cl\}_2$, 25966-16-9; $\{Ir(C_8H_{12})Cl\}_2$, 12112-67-3; $\{Rh(CO)_2Cl\}_2$, 14523-22-9; $\{Rh(CO)_2SC_6H_5\}_2$, 24818-80-2.

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Single Hydrogen–Boron Bridged Species: Tris(methyldiphenylphosphine) Complexes of Silver(I) and Copper(I) Containing Tetrahydroborate and (Ethoxycarbonyl)trihydroborate

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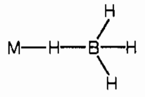
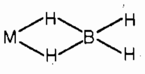
The complexes (tetrahydroborato)tris(methyldiphenylphosphine)copper(I), (tetrahydroborato)tris(methyldiphenylphosphine)silver(I), ((ethoxycarbonyl)trihydroborato)tris(methyldiphenylphosphine)copper(I), and ((ethoxycarbonyl)(trihydroborato)tris(methyldiphenylphosphine)silver(I) have been synthesized and characterized. IR data and analysis support the presence of a hydrogen singly bridged to the metal in the solid species. In solution, conductivity, molecular weight, and NMR data indicate the existence of equilibrium between singly and doubly bridged species. Factors influencing the formation of a singly bridged vs. a doubly bridged species are discussed.

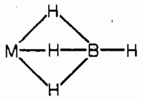
Recent communications have reported the existence of a single-hydrogen bridge attachment of tetrahydroborate to copper(I).[2,3] Of the three possible orientations I–III these are the only reports of type I with M = copper. In this paper, we report in detail the synthesis and characterization of four methyldiphenylphosphine complexes, the evidence for which suggests that a single-hydrogen bridge attachment of the boron-containing moiety to the metal is present. The complexes are (tetrahydroborato)tris(methyldiphenylphosphine)copper(I)



I



II



III

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