620. *π-Cyclopentadienyl- and Cyclopentadiene-iron Carbonyl Complexes.*

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Chloro-π-cyclopentadienyldicarbonyliron has been converted by the action of carbon monoxide and triphenyl-phosphine, -arsenine, or -stibine into the cationic species π-$C_5H_5Fe(CO)_3^+$ and [π-$C_5H_5Fe(CO)_2MPh_3]^+$ (where M = P, As, or Sb).

Reduction by sodium borohydride of the triphenylphosphine-substituted ion gives dicarbonylcyclopentadienetriphenylphosphineiron, but the tricarbonyl cation gives only hydridodicarbonyl-π-cyclopentadienyliron.

Infrared and nuclear magnetic resonance spectra are reported.

THE interaction of iron pentacarbonyl with cyclopentadiene or its dimer produces the binuclear carbonyl [π-$C_5H_5Fe(CO)_2]_2$,[1] and it has been suggested [2,3] that a cyclopentadiene olefin-type complex, $C_5H_6Fe(CO)_3$, is an intermediate in the preparation. An unsuccessful attempt [4] has been made to isolate such a complex from spiro[4,4]nona-1,3-diene, but rearrangement occurred producing tetracarbonyldi-π-tetrahydroindenyldi-iron.

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[1] For references see Wilkinson and Cotton, " Progress in Inorganic Chemistry," Interscience Publ. Inc., New York, 1959, Vol. I, p. 1.

[2] Sternberg and Wender, Int. Conf. Co-ordination Chem., London, 1959, *Chem. Soc. Special Publ.*, No. 13, p. 35.

[3] Pauson, *Proc. Chem. Soc.*, 1960, 297.

[4] Hallam and Pauson, *J.*, 1958, 646.

We have previously shown [5] that suitable π-cyclopentadienylmetal cations can be reduced by lithium aluminium hydride or sodium borohydride to give cyclopentadiene olefin-type complexes, *e.g.*, $\pi\text{-}C_5H_5CoC_5H_6$. It seemed reasonable to expect that if cations such as $\pi\text{-}C_5H_5Fe(CO)_3^+$ could be obtained, their reduction by hydride ion should lead to the corresponding olefin complexes;

$$\pi C_5H_5FeL_n^+ + H^- = C_5H_6FeL_n$$

π-Cyclopentadienylcarbonyliron Cations.—Cations of this type have not been reported previously, although the yellow aqueous solutions of $\pi\text{-}C_5H_5Fe(CO)_2Cl$ undoubtedly contain the ion $[\pi\text{-}C_5H_5Fe(CO)_2H_2O]^+$.[1] If the dicarbonyl chloride in acetone solution in the presence of sodium tetraphenylborate is treated with carbon monoxide under pressure, fine yellow crystals of the tetraphenylborate of the ion $\pi\text{-}C_5H_5Fe(CO)_3^+$ are obtained in almost quantitative yield:

$$\pi\text{-}C_5H_5Fe(CO)_2Cl + NaBPh_4 + CO = \pi\text{-}C_5H_5Fe(CO)_3[BPh_4] + NaCl$$

The tetraphenylborate decomposes only slowly in air; it is insoluble in non-polar solvents and is sparingly soluble in acetone from which it crystallises with difficulty. It decomposes without melting when heated. Conductivity measurements in nitrobenzene [6] show that it is a 1 : 1 electrolyte. The ion completes the isoelectronic series [1] $[\pi\text{-}C_5H_5V(CO)_3]^{2-}$, $[\pi\text{-}C_5H_5Cr(CO)_3]^{1-}$, $\pi\text{-}C_5H_5Mn(CO)_3$.

Since other ligands, particularly tertiary phosphines, could be expected to act similarly to carbon monoxide in the above reaction, we have re-examined the interaction of $\pi\text{-}C_5H_5Fe(CO)_2Cl$ and triphenylphosphine [7] which gave a small yield of $(Ph_3P)_2Fe(CO)_3$. This observation has been confirmed, but we have found that if the benzene-insoluble portion of the reaction mixture is extracted with water, a solution of $[\pi\text{-}C_5H_5Fe(CO)_2PPh_3]^+$ is obtained from which the chloride can be isolated as a trihydrate. This yellow solid decomposes without melting; it is sparingly soluble in cold water but readily soluble in hot water. Aqueous solutions give the usual precipitation reactions with large anions, and conductivity measurements in nitrobenzene showed that the chloride is a 1 : 1 electrolyte and the hexachloroplatinate(IV) a 1 : 2 electrolyte. Similar salts were characterised with triphenylarsine and triphenylstibine as ligands, but these are less stable in air than the very stable phosphine derivatives.

The infrared spectra of the isoelectronic π-cyclopentadienyl tricarbonyl compounds, $Cs_2[\pi\text{-}C_5H_5V(CO)_3]$, $Na[\pi\text{-}C_5H_5Cr(CO)_3]$, $\pi\text{-}C_5H_5Mn(CO)_3$, and $[\pi\text{-}C_5H_5Fe(CO)_3][BPh_4]$, show two strong bands due to terminal C–O stretching modes. The formal oxidation state of the metals in this series are V(−1), Cr(0), Mn(+1), and Fe(+2). The values of the C–O stretching frequencies can be interpreted as showing the degree of electron-transfer from the metal orbitals into vacant orbitals of the carbon monoxide by metal–carbon π-bonding. The stretching frequencies for this series are: 1748, 1645; 1876, 1695; 2035, 1953; [8a] and 2120, 2070 cm.$^{-1}$. These show the expected increase in π-bonding with increasing negativity of the oxidation state (Fe $\longrightarrow$ V) of the central metal atom in a manner analogous to that of the N–O stretching frequencies in the isoelectronic series $K_2[Fe(CN)_5NO]$, $K_3[Mn(CN)_5NO]$, $K_5[V(CN)_5NO]$.[8b] In the triphenyl-phosphine, -arsine, and -stibine complexes the carbonyl stretching modes occur at 2070, 2030; 2062, 2017; and 2005, 2050 cm.$^{-1}$, respectively. The lowering of these values from 2120 cm.$^{-1}$ for the tricarbonyl to about 2060 cm.$^{-1}$ for the phosphorus, arsenic, and antimony compounds may be associated with decreasing π-bonding capacity here, with a resultant increase in π-bonding between

[5] Green, Pratt, and Wilkinson, *J.*, 1959, 3753.

[6] Nyholm and Morris, *J.*, 1956, 4375.

[7] Hallam and Pauson, *J.*, 1956, 3030.

[8] (*a*) Fischer, *Chem. Ber.*, 1960, **93**, 165; (*b*) Griffith, Lewis, and Wilkinson, *J.*, 1959, 1632; (*c*) Abel, Bennett, and Wilkinson, *J.*, 1959, 2323; Chatt and Hart, *J.*, 1960, 1378.

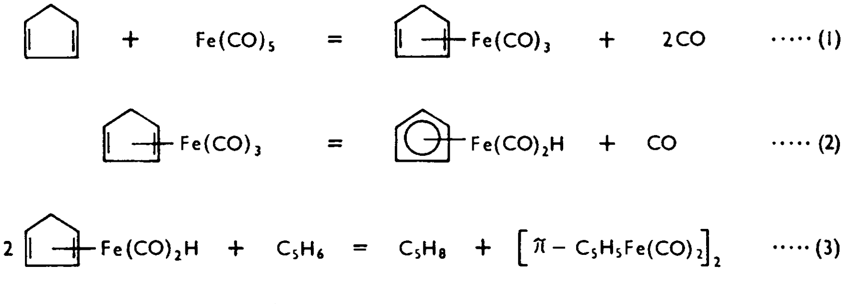
metal and carbon monoxide. The C–O frequencies increase in the order $SbPh_3 < AsPh_3 < PPh_3$ but the differences are small, *ca.* 12 cm.$^{-1}$, and are probably of little real significance except that they confirm the observations [8c] that there is little difference in π-acceptor properties of phosphorus, arsenic, and antimony as ligand atoms.

Dicarbonylcyclopentadienetriphenylphosphine iron.—Although we have failed to obtain a cyclopentadiene derivative by reduction of the ion $[\pi\text{-}C_5H_5Fe(CO)_3]^+$, reduction of the triphenylphosphine derivative, $[\pi\text{-}C_5H_5Fe(CO)_2PPh_3]Cl$, by sodium borohydride in tetrahydrofuran–ether gives the olefin-type complex, $C_5H_6Fe(CO)_2PPh_3$.

The physical and chemical properties of dicarbonylcyclopentadienetriphenylphosphine iron show that cyclopentadiene is bound to the iron atom in the same manner as in the cobalt and rhodium compounds,[5] and that the methylene group ($>CH_\alpha H_\beta$) of the cyclopentadiene has the same unusual features as before. The compound decomposes appreciably when left in air but is stable in nitrogen or *in vacuo* at room temperature. With carbon tetrachloride it reacts, to give chloroform and the $\pi\text{-}C_5H_5Fe(CO)_2PPh_3^+$ ion. In boiling xylene the compound decomposes to give $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ and a small amount of ferrocene (which probably results from the decomposition of the binuclear carbonyl in xylene [7]). Interaction between the compound and triphenylmethyl tetrafluoroborate is very slow, the reactive H_α being removed essentially quantitatively to give the crystalline salt $[\pi\text{-}C_5H_5Fe(CO)_2PPh_3]BF_4$; the infrared spectrum of the latter is consistent with formulation as an ionic tetrafluoroborate.[9]

The infrared spectrum of $C_5H_6Fe(CO)_2PPh_3$ shows an intense band at 2765 cm.$^{-1}$ assignable to the C–H_α stretching mode; other assignments are also similar to those of other cyclopentadiene derivatives.[5] The high-resolution nuclear magnetic resonance spectrum is also similar in its general features to those of the other derivatives.[5] Thus there are three groups of lines in the spectrum, indicating the presence of at least three types of hydrogen atom. A sharp doublet (τ 2·73, relative intensity 15) is clearly due to the protons of the triphenylphosphine portion, the proton line being split by coupling with the ^{31}P nuclear spin. The remaining lines are assignable as before. The band at τ 4·87 (relative intensity 2) from protons on $C_{(3)}$ and $C_{(4)}$, which appears as a triplet, should exist as a double doublet due to spin-coupling of each proton with those on $C_{(2)}$ and $C_{(5)}$, but this expected fine structure was not resolvable owing to overlapping of the bands. The third band at τ 7·5 (relative intensity 4) is due to the remaining protons on the C_5H_6 group. The lines at τ 7·19, τ 7·38, and τ 8·0 appear to be part of an AB pair due to the protons of the non-equivalent methylene group, $>CH_\alpha H_\beta$; the *endo*-proton, H_α, is in a different magnetic environment from that of the *exo*-proton H_β. The poorly resolved lines at τ 7·66 and τ 7·79 are due partly to H_α and to the protons on $C_{(2)}$ and $C_{(5)}$.

Discussion.—In the interaction of cyclopentadiene with iron pentacarbonyl, the following reactions have been proposed: [2,3]



It is known that $\pi\text{-}C_5H_5Fe(CO)_2H$, which is readily obtained by the action of sodium borohydride on $\pi\text{-}C_5H_5Fe(CO)_2Cl$, is thermally unstable, decomposing in the liquid state

[9] Sharp and Sheppard, *J.*, 1957, 674.

to give the binuclear carbonyl and hydrogen.[10] However, all our attempts to isolate $C_5H_6Fe(CO)_3$ by borohydride reduction of $[\pi\text{-}C_5H_5Fe(CO)_3]^+[BPh_4]^-$ in tetrahydrofuran failed, even at low temperatures, the reaction leading only to the dicarbonyl hydride with loss of carbon monoxide. It appears that $C_5H_6Fe(CO)_3$ is unstable with respect to $\pi\text{-}C_5H_5Fe(CO)_2H$ and that the transition-state activated complex $[\pi\text{-}C_5H_5Fe(CO)_2LH]$ ($L = CO$) decomposes by loss of carbon monoxide in preference to forming the neutral compound $C_5H_6Fe(CO)_3$. In the case where $L = PPh_3$, only a small amount of $\pi\text{-}C_5H_5Fe(CO)_2H$, which was detected by its high-field proton-resonance line and by its decomposition to $[\pi\text{-}C_5H_5Fe(CO)_2]_2$, is produced and the main product is the neutral cyclopentadiene complex. The latter is stable with respect to ligand-loss and hydrogen-transfer to metal to give $\pi\text{-}C_5H_5Fe(CO)_2H$, and there is no evidence of decomposition below 113° to $[\pi\text{-}C_5H_5Fe(CO)_2]_2$. Although the complex $C_5H_6Fe(CO)_3$ is unstable, there appears to be no inherent instability in diolefin-iron tricarbonyl systems and tricarbonyl compounds of norbornadiene, butadiene, cycloheptadiene, etc., are known, although these compounds do not contain a reactive $>CH_\alpha H_\beta$ group.

The readier loss of carbon monoxide in the reduction of $\pi\text{-}C_5H_5Fe(CO)_3^+$ than in that of the triphenylphosphine complex, and similar differences in reactivities between acylcobalt carbonyls and their triphenylphosphine analogues,[11] may be due to the non-volatility of triphenylphosphine and its weaker π-bonding capacity which tends to strengthen the remaining Fe–C bonds.

Our observations thus appear to be consistent with the above reaction scheme, but further studies to elucidate the mechanism of hydrogen-transfer are in progress.

EXPERIMENTAL

Microanalyses and molecular weights (ebullioscopic in benzene) are by the Microanalytical Laboratories, Imperial College.

Tricarbonyl-π-cyclopentadienyliron Tetraphenylborate.—*Method* 1. Chlorodicarbonyl-π-cyclopentadienyliron (0·5 g.) and sodium tetraphenylborate (0·85 g.) were dissolved in anhydrous acetone (2—3 ml.). The solution was placed in a small autoclave with carbon monoxide (90 atm.; 25—30°) for 48 hr. The product crystallised in the autoclave as large golden-yellow triangular plates; these were crushed and washed with air-free water. Recrystallisation from acetone at −78° and drying in a vacuum gave the yellow *complex*, decomp. >184° (1·07 g., 85%) (Found: C, 73·3; H, 5·0; O, 9·5. $C_{32}H_{25}BFeO_3$ requires C, 73·35; H, 4·8; O, 9·2%). The crystals slowly darken in air; they are insoluble in water, ether, alcohol, benzene, and light petroleum but soluble in acetone and nitrobenzene [conductance in nitrobenzene ($1·08 \times 10^{-3}$M), $\Lambda = 22·8$ ohm^{-1} at 23°].

Method 2. The chloro-compound (0·509 g.) and sodium tetraphenylborate (0·903 g.) in acetone (3 ml.) were held at 25° under nitrogen for 6 days; the product gave yellow plates (0·157 g., 12·6%). The formation of the salt under these conditions must involve intermolecular transfer of carbon monoxide.

Chlorodicarbonyl-π-cyclopentadienyltriphenylphosphineiron Trihydrate.—*Method* 1. Chlorodicarbonyl-π-cyclopentadienyliron (1·3 g.) and triphenylphosphine (2·5 g.) in tetrahydrofuran (20 ml.) were heated under reflux until a vigorous reaction set in (*ca.* 5 min.) and a brown solid separated; heating was continued for a further 5 min. Filtration gave a brown amorphous powder which was extracted with hot water (2 × 10 ml.); the filtrate, on cooling, deposited yellow crystals. Repeated crystallisation from hot water and drying in a vacuum-desiccator gave a golden-yellow *trihydrate*, decomp. >120° (0·93 g., 30%) (Found: C, 56·7; H, 4·9; P, 5·8; Cl, 6·7; Fe, 10·4. $C_{25}H_{20}ClFeO_2P,3H_2O$ requires C, 56·8; H, 4·9; P, 5·9; Cl, 6·7; Fe, 10·6%). The salt is stable in air and readily soluble in hot but sparingly soluble in cold water. All the chloride is ionic and can be precipitated with silver ion. Addition of chloroplatinic acid to a solution gives a white precipitate of the *chloroplatinate* (Found: C, 46·2; H, 3·3; Cl, 16·6. $C_{50}H_{40}Cl_6Fe_2O_4P_2Pt$ requires C, 46·6; H, 3·1; Cl, 16·5%). Ammonium

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[10] Green, Street, and Wilkinson, *Z. Naturforsch.*, 1959, **14**b, 738.

[11] Heck and Breslow, *J. Amer. Chem. Soc.*, 1960, **82**, 750, 4438.

reineckate solution gave a pale pink *reineckate* which was crystallised from acetone–water (Found: C, 46·2; H, 3·6; N, 11·1. $C_{29}H_{26}CrFeN_6O_2P$ requires C, 46·0; H, 3·5; N, 11·1%). Bromine water gave a pale orange precipitate of the *tribromide*, which crystallised from chloroform (Found: C, 44·3; H, 3·2. $C_{25}H_{20}Br_3FeO_2P$ requires C, 44·2; H, 2·9%). In nitrobenzene at 23°, $0·83 \times 10^{-3}$M-π-$C_5H_5Fe(CO)_2PPh_3Cl,3H_2O$ had Λ 19·56 ohm^{-1}; $1·02 \times 10^{-3}$M-[π-$C_5H_5Fe(CO)_2PPh_3]_2PtCl_6$ had Λ 37·6 ohm.$^{-1}$.

Method 2. Equivalent amounts of the chloride reactant and triphenylphosphine were heated in a sealed tube.[7] Extraction of the product with benzene and chromatography on alumina gave tricarbonylbistriphenylphosphineiron, m. p. 272—275° (decomp.), in low yield. Extraction of the benzene-insoluble matter with hot water gave a yellow solution from which the cation was precipitated as the reineckate which crystallised as above (Found: C, 46·5; H, 3·6: N, 10·9%).

Triphenyl-arsine and -stibine Analogues.—The triphenylarsine and triphenylstibine cations could be prepared only by the sealed-tube method above. They were precipitated from their aqueous solutions as the *hexachloroplatinates* (Found: C, 43·2; H, 3·4; O, 5·1; Cl, 16·0. $C_{50}H_{40}As_2Cl_6Fe_2O_4Pt$ requires C, 43·6; H, 2·9; O, 4·7; Cl, 15·5%. Found: C, 41·0; H, 3·3; O, 5·3. $C_{50}H_{40}Cl_6Fe_2O_4PtSb_2$ requires C, 41·0; H, 2·8; O, 4·4%). They are less stable in air than the triphenylphosphine complex.

Dicarbonylcyclopentadienetriphenylphosphineiron.—Chlorodicarbonyl-π-cyclopentadienyltriphenylphosphine iron trihydrate (1·5 g.) was suspended in 2 : 1 tetrahydrofuran–ether (40 ml.) at *ca.* −10° under nitrogen and treated with small portions (*ca.* 0·25 g.) of sodium borohydride until the suspended salt was completely dissolved (*ca.* ½ hr.) and the solution was yellow. [This solution showed a weak high-field proton-resonance line identical with that of π-$C_5H_5Fe(CO)_2H$.] The solution was treated with air-free water (100 ml.) and extracted with light petroleum (b. p. 30—40°; 50 ml.). The petroleum layer [which rapidly darkened even under nitrogen owing to decomposition of π-$C_5H_5Fe(CO)_2H$] was washed with water, dried ($CaCl_2$), and concentrated to low bulk at 20°/2 mm. Chromatography on alumina (Brockmann, grade 3) under nitrogen gave a yellow weakly absorbed band which was rapidly eluted with ether and a dark red-brown strongly absorbed band from which, after extrusion, tetracarbonyldi-π-cyclopentadienyldi-iron was extracted with acetone (0·08 g., 7—8%; m. p. and mixed m. p. 193—194°). After removal of solvent from the yellow eluate at 20°/0·2 mm. a yellow solid (0·9 g., 75%) remained. Crystallisation from light petroleum (b. p. 30—40°) at −78° gave a golden-yellow *complex*, m. p. 113—114° (decomp.) (Found: C, 68·2; H, 4·8; P, 7·4; Fe, 12·4%; *M*, 420. $C_{25}H_{21}FeO_2P$ requires C, 68·25; H, 4·8; P, 7·05; Fe, 12·7%; *M*, 440). The compound decomposes within a few hours in air. On melting, it evolves a non-condensable gas and leaves a red oil. It is readily soluble in non-polar solvents, and the solutions darken over a period of days in absence of oxygen. Solutions in carbon disulphide begin to darken after 1 hr., whilst in carbon tetrachloride rapid decomposition (*ca.* 1 min.) occurs, producing chloroform and π-$C_5H_5Fe(CO)_2PPh_3Cl$, which was isolated as the chloroplatinate. The compound is moderately stable (*ca.* 1—2 days) in dichloromethane.

Thermal Decomposition of $C_5H_6Fe(CO)_2PPh_3$.—A solution of the compound (0·23 g.) in xylene (4—5 ml.) was heated under reflux for 5 min. After 1 min. the solution became deep red-brown. Chromatography with benzene eluate allowed the isolation of ferrocene, m. p. 171—173°; the compound [π-$C_5H_6Fe(CO)_2]_2$ (0·052 g., 60%), m. p. and mixed m. p. 189—192°, was recovered from the column by extraction with acetone.

Abstraction of Hydrogen from $C_5H_6Fe(CO)_2PPh_3$.—Triphenylmethyl tetrafluoroborate (0·15 g.) in dichloromethane (1—2 ml.) was added to a solution of the compound (0·123 g.) in dichloromethane (2 ml.). The reaction is only slow; after 12 hr. at *ca.* 5° the yellow crystals of *π-cyclopentadienyldicarbonyltriphenylphosphineiron tetrafluoroborate* were removed, washed with solvent and dried (0·102 g., 69%), decomp. >250° (Found: C, 56·0; H, 4·4. $C_{25}H_{20}BF_4FeO_2P$ requires C, 56·9; H, 3·8%).

Reduction of [π-$C_5H_5Fe(CO)_3][BPh_4]$.—A suspension of the salt (2·4 g.) in tetrahydrofuran (50 ml.) at −20° under nitrogen, on treatment with sodium borohydride, gave a deep yellow solution. This solution, which is similar in appearance to that obtained by reduction of π-$C_5H_5Fe(CO)_2Cl$ under the same conditions, shows a strong proton-resonance line at a position identical with that given by π-$C_5H_5Fe(CO)_2H$. Treatment of the solution with air-free water followed by extraction with light petroleum (b. p. 30—40°) caused rapid darkening of the organic layer. After removal of solvent at *ca.* 0°/0·1 mm., there remained purple crystals of the compound $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ (0·62 g., 75%), m. p. and mixed m. p. 194°; some of the readily volatile yellow complex $\pi\text{-}C_5H_5Fe(CO)_2H$ condensed in the cold trap during removal of solvent, and on melting decomposed with effervescence to give more of the binuclear product.

This experiment has been repeated several times and no evidence for a cyclopentadiene compound has been obtained.

Other Reactions of $\pi\text{-}C_5H_5Fe(CO)_2Cl$.—Refluxing this compound in tetrahydrofuran for 15 hr. under nitrogen afforded ferrocene and ferrous chloride; this reaction also occurs when the chloride is heated at 220°.[7] If equivalent amounts of phenyl- or diphenyl-acetylene are added, the products are the same. The addition of 2,2′-bipyridyl or 1,10-phenanthroline causes complete disruption, resulting in octahedral ferrous complexes such as chlorotris-1,10-phenanthrolineiron(II).

High-resolution Nuclear Magnetic Resonance Spectra.—Spectra were measured on a Varian model 43100 instrument at 56·43 Mc./sec. with 5-mm. (outside diameter) spinning sample tubes; tetramethylsilane was added as an internal reference and shifts are given in τ-values. $C_5H_6Fe(CO)_2PPh_2$ (in benzene and CS_2) gave 2·73, doublet (5·2 cycles/sec), phenyl protons; 4·87, " triplet " (4·2 cycles/sec.), H_3, H_4; 7·18, 7·38, H_β, 7·66, part of H_α; 7·79, H_2,H_5; 8·0, part of H_α.

Infrared Spectra.—The spectra in hexachlorobutadiene and Nujol mulls were taken on a Perkin–Elmer model 21 instrument with calcium fluoride and sodium chloride optics where appropriate. The assignments listed (in cm.$^{-1}$) are (a) C–H phenyl, (b) C–H olefin, (c) C–H_β, (d) C–H_α, (e) C_6H_5 out-of-plane deformation on PPh_3, (f) the same on BPh_4^-, (g) and (h) the same on $AsPh_3$ and $SbPh_3$, respectively, (i) O–H stretch, (j) O–H deformation, (k) C–O stretch, (l) BF_4^- asymmetric stretch, (m) spectra in CS_2 solution.

$C_5H_6Fe(CO)_2PPh_3$^{m}: 3072w^{a}, 3010m^{b}, 2965w^{c}, 2765s^{d}, 1978vs^{k}, 1912vs^{k}, 1380vw, 1338vw, 1306vw, 1245vw, 1217w, 1186m, 1095m, 1073vw, 1055vw, 1030vw, 1000vw, 926vw, 830vw, 745s^{e}, 695s^{e}.

$[C_5H_5Fe(CO)_3][BPh_4]$: 3092vw, 3053vw; 2070vs^{k}, 2120vs^{k}; 1580w, 1477m, 1433m, 1425m, 1305w, 1184w, 1153w, 1145w, 1115w, 1067w, 1033w, 1016vw, 1004w, 876w, 849w, 747s^{f}, 709s^{f}.

$[C_5H_5Fe(CO)_2PPh_3]Cl,3H_2O$: 3320vs^{i}; 2030vs^{k}; 2066vs^{k}; 1635m^{j}, 1435m, 1308w, 1115w, 1095m, 1075vw, 998w, 875w, 745ms^{e}, 695s^{e}.

$[C_5H_5Fe(CO)_2PPh_3]_2PtCl_6$: 3080, 3100w; 2030vs^{k}, 2070s^{k}; 1432m, 1310w, 1115w, 1096m, 1070vw, 998w, 875w, 750ms^{e}, 693ms^{e}.

$[C_5H_5Fe(CO)_2AsPh_3]_2PtCl_6$: 2017vs^{k}, 2062vs^{k}; 1432m, 1303w, 1183vw, 1155vw, 1073vw, 1018vw, 998w, 865vw, 740vs^{g}, 690s^{g}.

$[C_5H_5Fe(CO)_2SbPh_3]_2PtCl_6$: 2005vs^{k}, 2050vs^{k}; 1475m, 1435m, 1304vw, 1180vw, 1155vw, 1065vw, 1017vw, 997w, 874vw, 734ms^{h}, 690ms^{h}.

$[C_5H_5Fe(CO)_2PPh_3]BF_4$: 2033vs^{k}, 2069vs^{k}; 1484m, 1438m, 1316w, 1288w, 1192w, 1172w, 1075vs^{l}, 873w, 750s^{e}, 695s^{e}.

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