Mixed metal clusters of iron and cobalt from carbonyl iron dichloro-phenylphosphine complexes with cyclopentadienyl cobalt dicarbonyl

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The reaction of CpCo(CO)₂ with the monoiron carbonyl phosphine complexes, Fe(CO)₅PPhCl₂ and the two diiron carbonyl phosphine complexes, Fe₂(CO)₆(PPhCl)₂, Fe₂(CO)₆(PPh₂)₂ have been studied which yields the heterometallic phosphorus bridged cluster molecules (CpCo)₂Fe(CO)₆(PPh) (1) and (CpCo)₂Fe(CO)₆(PPh₂) (2), (CpCo)Fe₂(CO)₆(PPh)₄ (3) and (CpCo)₂Fe₂(CO)₆(PPh₂)₃ (5), (CpCoFe₂(CO)₆PPh)₆ and (CpCo)₆Fe₂(CO)₆(PPh₃) (7) respectively. A homometallic complex (CpCo)₄(PPh)₄ (3) is also obtained as a side product from the reaction with Fe(CO)₅PPhCl₂ only. All the products have been characterised by the analytical data and IR, ¹H-NMR and mass spectra.

Homo- and heterocycles consisting of transition metal functionalised phosphorus atoms fall between organometallic and main group element chemistry. The synthesis of phosphorus bridged polynuclear homo- and heterometallic cluster compounds through generation of new phosphorus – metal and metal – metal bonds have been successfully demonstrated by Huttner et al. and Vahrenkamp et al. One of the general reaction patterns of metallophosphines of the type [M]PPh₃ [M] = CpMo(CO)₅, CpW(CO)₅, CpFe(CO)₅, CpRu(CO)₅ involve the preparation of bimetallic phosphido-bridged complexes. However, the potentiality of π-cyclopentadienyl cobalt dicarbonyl, π-CpCo(CO)₂ towards phosphorus bridged polynuclear mixed metal cluster synthesis have not been thoroughly investigated. The tendency of π-CpCo(CO)₂ to undergo trimerisation via self decarbonylation to form [π-Cp(CO)]₃ may complicate the progress of the reactions and dictate the product types whereby stabilisation of the partially / totally decarbonylated cluster molecules or those with bridging CO-groups cannot be ruled out.

Experimental

Iron pentacarbonyl, Fe(CO)₅; π²-cyclopentadienyl-cobalt dicarbonyl, CpCo(CO)₅; dichlorophenylphosphine, PPhCl₂; triphenylphosphine, PPh₃ (Aldrich); lithiumaluminiumhydride, LiAlH₄ (E. Merck) were used as purchased. The organic solvents were dried, distilled and made saturated with nitrogen before use. Statement of reaction temperature means the outer hot and cold bath temperatures. Silica gel-60 was made water free at 160°C under vacuum and used for column chromatography. The eluents were not distilled but dried on fresh sodium pieces / wire for two days before use. Melting points were determined in capillaries under nitrogen. Metal contents were determined by spectrophotometric methods after decomposing the compounds with either fuming HNO₃ or H₂O₂/HClO₄.

Elemental analysis of C, H, N were performed on a Perkin-Elmer CHN analyser. Mass spectra were recorded on JEOL SX 102 / DA-6000, MICROMASS QUATTRO II triple quadrupole or JEOL D-300 spectrometers. Infrared spectra (KBr disc) were measured on a Perkin-Elmer FTIR PARAGON – 1000 spectrometer. ¹H-NMR spectra were recorded on either JEOL FX – 100 FT or BRUCKER DRX – 300 spectrometers. All reactions and handling of chemicals were performed under nitrogen atmosphere.

Carbonyl iron phenylchlorophosphine complexes, Fe(CO)₅PPhCl₂, Fe₂(CO)₆(PPhCl)₂ and Fe(CO)₅(PPhCl)₂ were prepared by the reactions between Fe(CO)₅ and PPhCl₂ as described in the literature.

Reactions of CpCo(CO)₅:

(a). With Fe(CO)₅PPhCl₂

Fe(CO)₅PPhCl₂ (1.39g, 4 mmol) dissolved in 30 ml benzene was slowly added to CpCo(CO)₅ (1.80g, 10 mmol) in 30 ml benzene with constant stirring. The mixture was then warmed and refluxed for ~6h, cooled to room temperature and filtered off. (CpCo)₂Fe(CO)₅PPh (1) was obtained as brown residue, purified by washing with pet. ether (petroleum ether, 60-80° and dried in vacuo. Yield 0.46g, (22%), m.p. 220°C(dec.). Found : C, 45.21; H, 2.74; Fe, 10.92; Co, 21.99 %. Calcd. for C₃₂H₃₄O₅PCoFe : C, 45.81; H, 2.89; Fe, 10.68; Co, 22.50 %. v(CO): 1969(vs), 1910(s), 1830(m) cm⁻¹.

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The yellowish brown oil which was identified as the unreacted CpCo(CO)₂. Fraction 2 was eluted with pet. ether: benzene (3:1, v/v), the reddish-brown fraction so obtained was removed with all solvent and a dark-red solid mixed with some reddish-brown oil was obtained. The product (CpCo)₂Fe(CO)₅PPh (2) was washed with pet.ether: benzene (5:1, v/v), pet. ether, and dried in vacuo. Yield, 0.24g (11%); m.p., 211°C (dec.). Found: C, 45.10; H, 2.64; Fe, 9.95; Co, 20.97%. Caled. for C₂₃H₂₁O₅P₂FeC₀₂: C, 45.66; H, 2.74; Fe, 10.12; Co, 21.36%. v(CO): 2038(m), 1973(vs), 1910(w) cm⁻¹.

Fraction 3 was eluted with pet. ether: benzene (1:1, v/v). The dark brown colour fraction on removal of all solvent yielded (CpCo)₂{(PPh)₂} (3) as a dark brown solid which was purified by washing with pet. ether: benzene (1:1, v/v), pet. ether, and dried in vacuo. Yield, 0.33g (14%); m.p., 24°C (dec.). Found: C, 53.56; H, 4.33; Co, 32.87%. Caled. for C₂₃H₂₁O₅P₂FeC₀₂: C, 53.94; H, 4.25; Co, 33.91%. δ(Cp/J): 4.76(dd, 20H) ppm/198 Hz δ(Ph): 7.49(m,10H) ppm. FAB(pos.)MS, m/z: 712(=M⁺), 550([CpCo₂PPh]⁺), 350([CpCoPPh]⁺), 160([CpCoP]⁺), 58(=Co⁺), 31(=P⁺).

(b) With Fe₄(CO)₁₀(PPhCl)₄

Fe₄(CO)₁₀(PPhCl)₄ (1.71g, 3 mmol) dissolved in 40 ml benzene was added to CpCo(CO)₂ (1.10g, 6 mmol) in 20 ml benzene. The mixture was slowly warmed and the refluxed for 6h, cooled to room temperature and filtered off to remove the small amount of residue as undissolved materials. The filtrate on reduction of volume to ~15 ml was subjected to chromatographic separation on a silica-gel column.

Fraction 1 was a pale yellow solution obtained by eluting with pet. ether. was removed with all solvent and an oily red product identified as unreacted CpCo(CO)₂ was recovered. Fraction 2 was a dark-brown solution obtained by eluting with pet. ether: benzene (5:1, v/v), on removal of all solvents and washing with pet. ether: methylenechlordi (5:1, v/v) and pet. ether yielded (CpCo)₂Fe(CO)₅{(PPh)₃} (4) as a dark-brown, almost black solid. Yield, 0.46g (26%); m.p., 221°C (dec.). Found: C, 49.10; H, 3.15; Fe, 9.41; Co, 18.96%. Caled. for C₂₃H₂₃O₇FeC₇O₇: C, 49.68; H, 3.34; Fe, 9.24; Co, 19.52%. v(CO): 2049(s), 1994(m) cm⁻¹. δ(Cp/J): 4.70(dd,10H) ppm/2.2 Hz δ(Ph): 7.47(m,10H) ppm. FAB(pos.)MS, m/z: 604(=M⁺), 517([CpCo₂Fe(CO)₅PPh]⁺), 328([FeC₇O₇PPh]⁺), 251([CpCo₂FePh]⁺), 77(=Ph⁺), 59(=Co⁺). Fraction 3 was a pale red solution obtained by eluting with pet. ether: benzene (2:1, v/v), on removal of all solvent and washing with pet. ether: methylenechloride (3:1, v/v) yielded (CpCo)₂Fe(CO)₅{(PPh)₀} (5) as a brownish red solid. Yield, 0.67g (30%); m.p., 205°C (dec.). Found: C, 45.77; H, 2.52; Fe, 14.88; Co, 15.17%. Caled. for C₂₃H₂₃O₇FeC₇O₇: C, 45.17; H, 2.71; Fe, 15.04; Co, 15.85%. v(CO): 2047(s) cm⁻¹. δ(Cp/J): 4.84(dd,10H)/2.2 Hz δ(Ph): 7.24(m,10H) ppm.
(c) With $Fe_2(CO)_3(PPhCl_2)$

$Fe_2(CO)_3(PPhCl_2)$ (1.61g, 3.5 mmol) dissolved in 40 ml benzene was added to $CpCo(CO)Cl_2$ (1.26g, 7 mmol) in 20 ml benzene and heated slowly and then refluxed for 6h. The mixture was cooled to room temperature and filtered off. $CpCoFe_2(CO)_4(PPh)$ (6) was collected as a yellowish brown solid, purified with pet. ether: benzene (1:1, v/v), pet. ether: methylene chloride (2:1, v/v), pet. ether and dried in vacuo. Yield, 0.53g.

Results and discussion

The reaction between $Fe_2(CO)_3$ and $PPhCl_2$ at $-60^\circ C$ (ref. 13) gives $Fe_2(CO)_3PPhCl_2$ and $Fe_2(CO)_3(PPhCl_2)$ as the main products in high and moderate yields respectively whereas $Fe_2(CO)_3(PPhCl_2)$ is formed as a side product in low yield. Again when $Fe_2(CO)_3$ and PPhCl_2 are allowed to react at $-90^\circ C$ (ref. 15), $Fe_2(CO)_3(PPhCl_2)$ is the only isolable product which however on treatment with excess of $Fe_2(CO)_3$ yields $Fe_2(CO)_3PPhCl_2$.

The mononuclear complex $Fe(CO)_3(PPhCl_2)$ and the two binuclear complexes $Fe_2(CO)_3(PPhCl_2)$ and $Fe_2(CO)_3(PPhCl_2)$ offer unique opportunity for further dehalogenation reactions with suitable carbonyls. e.g. $CpCo(CO)_2$ which under appropriate conditions may lead to the synthesis of a variety of phosphorus bridged mixed metal cluster compounds with enhanced nucularity.

All the three mixtures of $CpCo(CO)_2$ with $Fe_2(CO)_3PPhCl_2$, $Fe_2(CO)_3(PPhCl_2)$ and $Fe_2(CO)_3(PPhCl_2)$ react at room temperature and the progress of the reactions were followed by the IR spectra in the v(CO) region. As no reaction appear to have taken place after ~3h, the reaction temperature is increased slowly when occurrence of more and more reactions are apparent from the simultaneous appearance of new bands and disappearance of some bands belonging to the starting materials in the v(CO) region of the IR spectrum. For completion of the reactions, the reaction mixtures are allowed to reflux for 6h.

The reaction between $Fe(CO)_3PPhCl_2$ and $CpCo(CO)_2$ yields $CpCo(Fe(CO)_3PPh(1)$ and $CpCo(Fe(CO)_3PPh(2)$ with two cobalt, one iron and a bridging phosphorus atom forming the cluster frameworks in them. The tetracobalt cluster $(CpCo)(PPh)_2(3)$ with two bridging phosphorus atoms is however obtained as a side product. Anticipating temperature dependency of the reaction and plausible generation of stable higher nuclear species the same reaction is performed in boiling toluene when no new products but 1 and 3 only are obtained in better yields whereas 2 is not formed at all. The reaction between $Fe_2(CO)_3(PPhCl_2)$
and CpCo(CO)₂ yields the complexes (CpCo)ₓFe(CO)ᵧ(PPh)ₗ(4) with two cobalt, one iron and a bridging phosphorus atom and (CpCo)ₓFe₂(CO)ᵧ(PPh)ₗ(5) with two cobalt and two iron along with two bridging phosphorus atoms forming a tetrahedron and a octahedron framework respectively. The reaction between Fe₂(CO)ₘ(PPhCl₂) and CpCo(CO)₂ on the other hand yields CpCoFe₂(CO)ₘ(PPh)(6) with one cobalt, two iron and a phosphorus atom forming the cluster framework. The other product from the same reaction is (CpCo)ₓFeₘ(CO)ᵧ(PPh)ₗ(7) where two each of cobalt and iron and two phosphorus atoms are involved in forming the octahedron framework of cluster.

Further it has been observed that 2 undergoes irreversible CO elimination reaction when kept stirring in benzene under mild vacuum at 40°C and 1 is formed via cluster closing reaction. However, on stirring 1 under CO atmosphere no cluster closing reaction and formation of 2 occur.

The IR spectra of the compounds 1 and 2 show the presence of ν(CO) frequencies at 2200 – 1900 cm⁻¹ as expected for the presence of terminal CO groups. An additional band in the lower frequency region at 1850 – 1750 cm⁻¹ observed for 1 clearly indicate the presence of CO group / groups between the two metal centres whereas for the compound 3, no ν(CO) band is observed suggesting the absence of any CO group.

The ¹H-NMR spectra indicates the presence of cyclopentadienyl rings (δ, 4.5 – 4.6 ppm, d) and the phenyl groups (δ, 7.4 – 7.6 ppm, m) for all the three compounds 1 to 3. The presence of doublets with low J values in the Cp-region of the spectrum suggest (at least slightly) different orientations of the Cp-rings and the presence of Cp-rings as cis- to each other is being proposed for 1 to 3.

In the IR spectra of 4 and 5, the ν(CO) frequencies appear in the range 2100 – 1900 cm⁻¹ suggesting the presence of only terminal CO-groups and the ¹H-NMR spectra show bands at δ, 4.85 – 4.65 ppm and at δ, 7.65 – 7.55 ppm, (m) corresponding to Cp- and Ph-

Molecular ion peaks, M⁺ along with the other assignable prominent peaks showed in the mass spectral fragmentation patterns convincingly support the molecular compositions of the products.

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