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Preliminary communication

PENTAMETHYLCYCLOPENTADIENYLCOPPER: A METAL LIGAND FRAGMENT ISOLOBAL WITH METHYLENE

GABINO A. CARRIEDO, JUDITH A.K. HOWARD, and F. GORDON A. STONE
Department of Inorganic Chemistry, The University of Bristol, Bristol BS8 1TS (Great Britain)

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Summary

Treatment of copper(I) chloride with LiC_5Me_5 in tetrahydrofuran affords a reagent which is a useful source of the $Cu(\eta\text{-}C_5Me_5)$ fragment in synthesis.

An appreciation of isolobal relationships between the organic species CH_3, CH_2 and CH and various metal-ligand fragments, a concept developed by Hoffmann [1], has allowed us to carry out several designed syntheses of organometallic complexes [2]. One direction of our work concerns isolobal mapping of CH_2 with the fragments $Cr(CO)_5$ (ML_5, d^6), $Rh(CO)(\eta\text{-}C_5Me_5)$, $Fe(CO)_4$ (ML_4, d^8), and $Pt(PR_3)_2$ (ML_2, d^{10}) [3]. The frontier orbitals of these metal-ligand fragments are descendants of an octahedral t_{2g} set [1] and a similar analysis of $Cu(\eta^5\text{-}C_5Me_5)$ (ML_3, Cu^I d^{10}) shows that this group is also isolobal with methylene. Hence a source of the copper species should allow "carbene-like" chemistry of $Cu(\eta^5\text{-}C_5Me_5)$ to be developed, provided kinetic factors are favourable [4].

Addition of copper(I) chloride to a tetrahydrofuran suspension of LiC_5Me_5 at −78°C affords a highly reactive dark yellow reagent presumed to be the complex $[Cu(thf)(\eta\text{-}C_5Me_5)]$ (I)*. Treatment of the latter with the compounds PPh_3, $[W\{=C(OMe)R\}(CO)_5]$ ($R = C_6H_4Me\text{-}4$), $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ ($R = C_6H_4Me\text{-}4$), or $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ gives the complexes IIa—Va, respectively. Also depicted are known compounds isolobal with these species, viz. IIb [6], IIIb [7], IVb [8], IVc [9], Vb [3a], and Vc [3a, 10].

The existence of IVa and IVb suggested the synthesis of the "mixed" trimetal complex VI. We have prepared the latter by treating I with $[PtW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$ [11].

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*It is possible that this thermally unstable solution contains copper-copper bonded species, e.g. $[Cu_2(\eta\text{-}C_5Me_5)_2]$ isolobal with $[Fe_2(CO)_8]$ or $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$, but the presence of the mononuclear pentamethylcyclopentadienylcopper tetrahydrofuran adduct seems more likely in view of the existence of related unstable complexes, e.g. $[Cu(CO)(\eta\text{-}C_5H_5)]$ [5].

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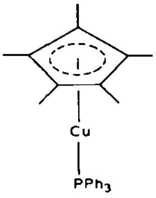
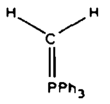
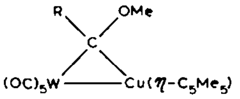


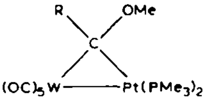
(IIa)



(IIb)



(IIIa)



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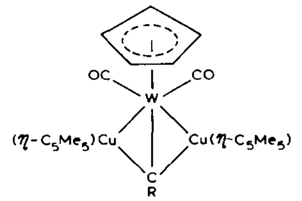
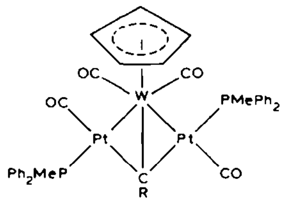
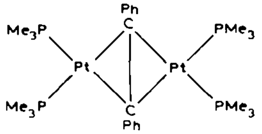


(IVa)

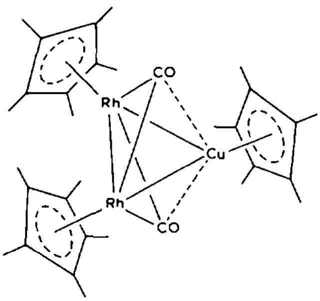


(IVb)

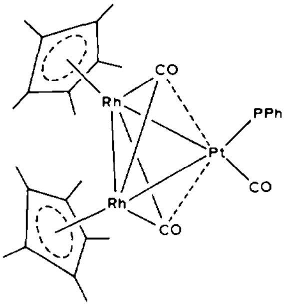


(IVc)

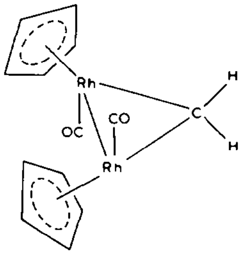
The spectroscopic properties of the new compounds are in accord with the structures proposed. Moreover, single-crystal X-ray diffraction studies have been carried out on Va and VI*. While diffraction data for the former reveal a solid state positional disorder of the metal atoms, the triangular arrange-



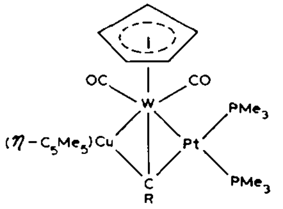
(Va)



(Vb)



(Vc)



(VI)

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*Crystal data for Va: $C_{32}H_{45}O_2CuRh_2$, $M = 731.0$, Orthorhombic, $a = 15.50(4)$, $b = 11.146(5)$, $c = 18.07(2)$ Å, $Z = 4$, $D_c = 1.56$ g cm^{-3}, $U = 3122$ Å^3, $F(000) = 1444$, space group $Pca2_1$ (No. 29), Mo-K_α X-radiation (graphite nonochromator), $\bar{\lambda} = 0.71069$ Å, μ(Mo-K_α) = 17.3 cm^{-1}. $R(R')$ 0.095 (0.079) for 1022 intensities with $I > 0.5\sigma(I)$.

*Crystal data for VI: $C_{31}H_{45}O_2P_2CuPtW$, $M = 954.1$, Monoclinic, $a = 10.516(5)$, $b = 17.898(8)$, $c = 18.134(6)$ Å, $\beta = 94.25(3)°$, $Z = 4$, $D_c = 1.87$ g cm^{-3}, $U = 3403$ Å^3, $F(000) = 1831$, space group $P2_1/c$ (No. 14), μ(Mo-K_α) = 83.3 cm^{-1}.

ment of the $CuRh_2$ ring (mean M—M 2.56(1) Å), the pentahapto coordination of the η-C_5Me_5 ligands, and the presence of two semi-μ_3 bridging CO groups, have been established. The structure of VI is shown in Fig. 1. The CuPtW(μ-C) atoms adopt a "butterfly" configuration with the copper and platinum occupying the wing-tips (dihedral angle 89.7°). The Cu—Pt separation (2.807(3) Å) is longer than the sum of the covalent radii (2.47 Å) indicating the absence of any significant bonding between these atoms. The Pt—Pt separation in species with structures IVb and IVc also correspond to little or no direct metal—metal bonding [8,12].

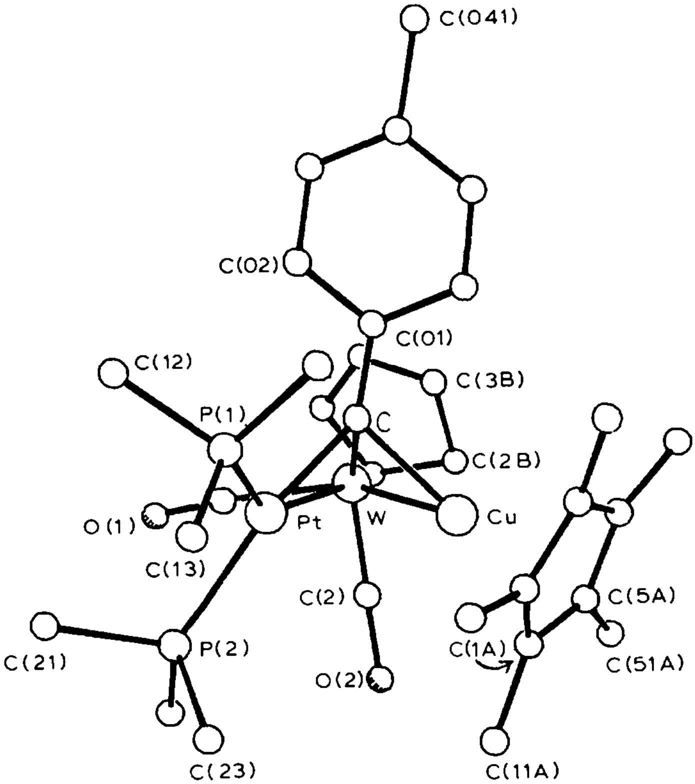

Fig. 1. The molecular structure of $[CuPtW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$. Selected internuclear separations and angles: Cu—Pt, 2.807(3); Cu—W, 2.648(3); Pt—W, 2.779(1); C—Cu, 1.96(2); C—Pt, 2.00(2); C—W, 2.03(2); P(1)—Pt, 2.285(6); P(2)—Pt, 2.341(7) Å; angle W—C(1)—O(1), 163 angle; W—C(2)—O(2), 171°.

From the results described herein, evidently I is a useful new reagent for organocopper chemistry, while an appreciation of the isolobal relationship between Cu(η-C_5Me_5) and CH_2 provides a guideline for further syntheses.

Experimental

All manipulations were carried out under dry nitrogen, with solvents freshly distilled from appropriate drying agents.

Synthesis. A typical preparative procedure is illustrated by the synthesis of IIIa.

A mixture of C_5Me_5H (0.43 g, 3.16 mmol) and Bu^nLi (3.16 mmol in 2 ml hexane) in tetrahydrofuran (30 ml) was cooled to −75°C and then treated with CuCl (0.34 g, 3.5 mmol) with stirring. The compound $[W\{=C(OMe)\text{-}C_6H_4Me\text{-}4\}(CO)_5]$ (0.85 g, 1.85 mmol) was added, and the temperature of the mixture was slowly (1 h) raised to ambient. Volatile material was removed in vacuo and the residue extracted with light petroleum (5 × 30 ml). The extracts were filtered through Celite, concentrated to circa 10 ml, and cooled to give deep red purple microcrystalline (0.62 g, 51%) IIIa (Found: C, 44.0; H, 3.8; mol.wt. (mass spectroscop.), 656.6. $C_{24}H_{25}CuO_6W$ calcd.: C, 43.9; H, 3.8%; mol.wt. 656.6). IR, ν_{max} (CO) 2065s, 1990m, 1962s, 1942vs, and 1906vw cm^{-1} (hexane). NMR: ^1H, δ 7.0 ($(AB)_2$ system, 4 H, C_6H_4, $J(AB)$ 8), 3.52 (s, 3 H, OMe), 1.96 (s, 3 H, Me-4), 1.60 (s, 15 H, C_5Me_5); $^{13}C\{^1H\}$, δ (ppm) 231.5 (μ-C), 202.2 (CO, $J(WC)$ 134 Hz), 197.0 (CO, $J(WC)$ 122 Hz), 155.4 ($C^1(C_6H_4)$), 139.4, 129.4, 127.0 (C_6H_4), 108.3 (C_5Me_5), 65.1 (OMe), 21.2 (Me-4), 9.4 (C_5Me_5).

Spectroscopic data. IR measurements were made in hexane, NMR studies in $[^2H_6]$benzene or $[^2H_8]$toluene. Representative data are as follows: IVa (violet crystals), IR ν_{max} (CO) 1934s, and 1955m cm^{-1}; NMR: ^1H, δ 6.84 (m, 4 H, C_6H_4), 4.72 (s, 5 H, C_5H_5), 2.08 (s, 3 H, Me-4), 1.92 (s, 30 H, C_5Me_5); $^{13}C\{^1H\}$, δ (ppm), 275.5 (μ_3-C), 213.9 (CO, $J(WC)$ 166 Hz), 158.7 ($C^1(C_6H_4)$), 135.7, 129.7 (C_6H_4), 107.8 (C_5Me_5), 90.3 (C_5H_5), 21.3 (Me-4), 10.7 (C_5Me_5). Va (deep blue crystals), IR 1728s cm^{-1}; NMR: ^1H, δ 1.80 (s, 15 H, C_5Me_5), 1.68 (s, 30 H, C_5Me_5); $^{13}C\{^1H\}$, δ (ppm) at −50°C, 241.5 (t, CO, $J(RhC)$ 44 Hz), 105.8 (CuC_5Me_5), 100.4 (RhC_5Me_5), 10.9 (CuC_5Me_5), 9.4 (RhC_5Me_5). VI (dark red crystals), IR 1906s, and 1816m(br) cm^{-1}; NMR: ^1H, δ 6.91 (s, 4 H, C_6H_4), 4.87 (s, 5 H, C_5H_5), 2.22 (s, 3 H, Me-4), 2.13 (s, 15 H, C_5Me_5), 1.43 (d, 9 H, PMe, $J(PH)$ 8, $J(PtH)$ 20 Hz), 0.97 (d, 9 H, PMe, $J(PH)$ 9, $J(PtH)$ 37 Hz); $^{31}P\{^1H\}$, δ (ppm, rel. H_3PO_4 (85%) ext.) −20.2 (d, $J(PP)$ 5, $J(PtP)$ 4211 Hz) and −29.2 (d, $J(PP)$ 5, $J(PtP)$ 2720 Hz).

Crystal structure determinations. Diffracted intensities were collected at room temperature on small black crystals of Va and VI using a Nicolet P3m four-circle automated diffractometer. For VI 2682 independent intensities were recorded to $2\theta \leqslant 50°$ using the $\omega:2\theta$ scan technique. Of these reflections, 2245 (absorption corrected) had $I \geqslant 1\sigma(I)$. The structure was solved, and all non-hydrogen atoms were located by conventional heavy-atom and difference Fourier methods. Carbon, oxygen and hydrogen atoms were refined isotropically. The latter were included at calculated positions, "riding" on the parent C atoms, except for those on the positionally disordered (60/40%) η-C_5H_5 ring, which were not included in the model. Refinement by blocked-cascade least squares led to $R = 0.055$ ($R' = 0.046$).

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