

Preliminary communication

PENTAMETHYLCYCLOPENTADIENYL COPPER: A METAL LIGAND FRAGMENT ISOLOBAL WITH METHYLENE

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(Received January 13th, 1983)

Summary

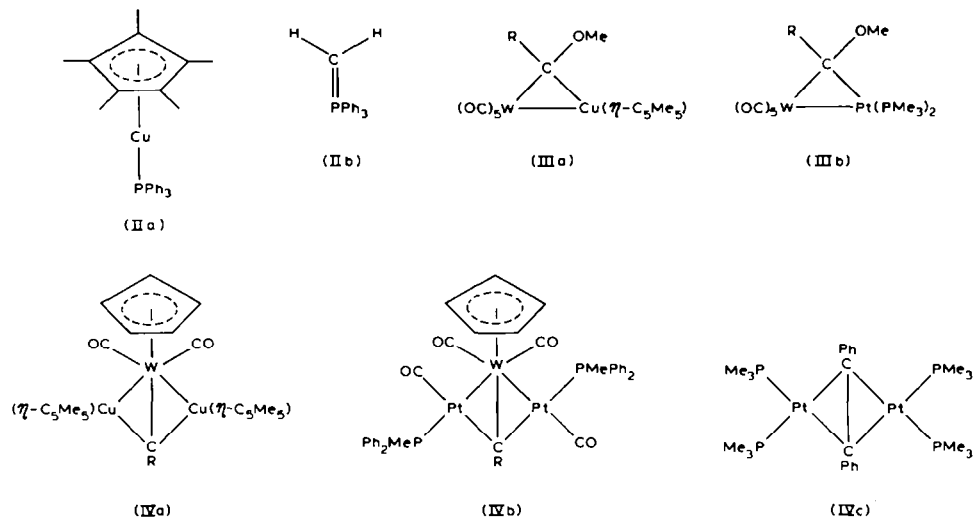
Treatment of copper(I) chloride with LiC_5Me_5 in tetrahydrofuran affords a reagent which is a useful source of the $\text{Cu}(\eta\text{-C}_5\text{Me}_5)$ fragment in synthesis.

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 $\text{Cr}(\text{CO})_5$ (ML_5 , d^6), $\text{Rh}(\text{CO})(\eta\text{-C}_5\text{Me}_5)$, $\text{Fe}(\text{CO})_4$ (ML_4 , d^8), and $\text{Pt}(\text{PR}_3)_2$ (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 $\text{Cu}(\eta^5\text{-C}_5\text{Me}_5)$ (ML_3 , $\text{Cu}^{\text{I}} d^{10}$) shows that this group is also isolobal with methylene. Hence a source of the copper species should allow "carbene-like" chemistry of $\text{Cu}(\eta^5\text{-C}_5\text{Me}_5)$ to be developed, provided kinetic factors are favourable [4].

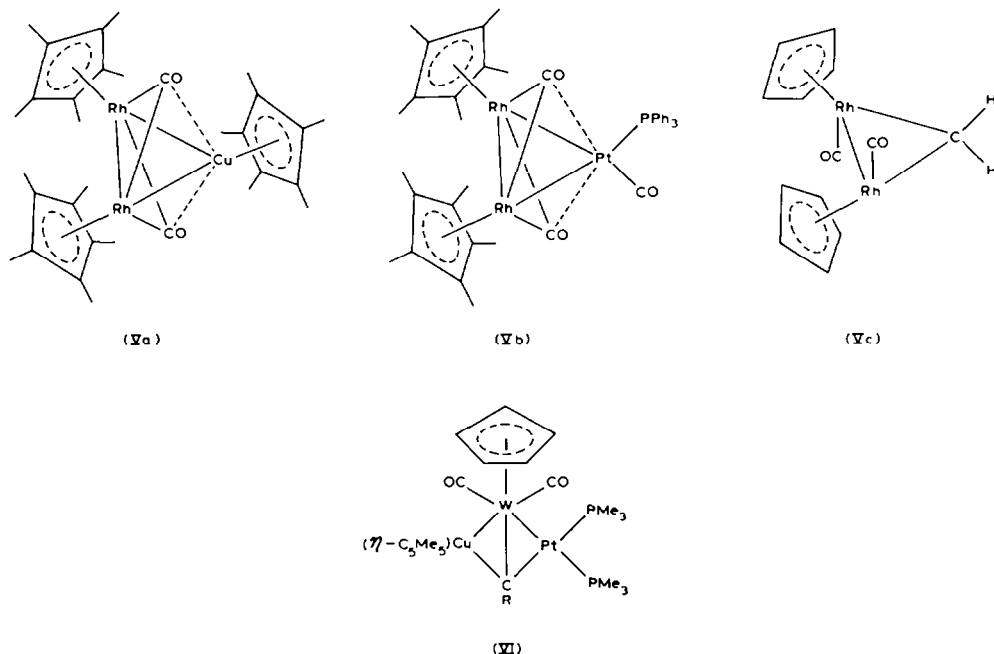
Addition of copper(I) chloride to a tetrahydrofuran suspension of LiC_5Me_5 at -78°C affords a highly reactive dark yellow reagent presumed to be the complex $[\text{Cu}(\text{thf})(\eta\text{-C}_5\text{Me}_5)]$ (I)*. Treatment of the latter with the compounds PPh_3 , $[\text{W}\{\equiv\text{C}(\text{OMe})\text{R}\}(\text{CO})_5]$ ($\text{R} = \text{C}_6\text{H}_4\text{Me-4}$), $[\text{W}(\equiv\text{CR})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ ($\text{R} = \text{C}_6\text{H}_4\text{Me-4}$), or $[\text{Rh}_2(\mu\text{-CO})_2(\eta\text{-C}_5\text{Me}_5)_2]$ 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 $[\text{PtW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\text{PMe}_3)_2(\eta\text{-C}_5\text{H}_5)]$ [11].

*It is possible that this thermally unstable solution contains copper-copper bonded species, e.g. $[\text{Cu}_2(\eta\text{-C}_5\text{Me}_5)_2]$ isolobal with $[\text{Fe}_2(\text{CO})_8]$ or $[\text{Rh}_2(\mu\text{-CO})_2(\eta\text{-C}_5\text{Me}_5)_2]$, but the presence of the mononuclear pentamethylcyclopentadienylcopper tetrahydrofuran adduct seems more likely in view of the existence of related unstable complexes, e.g. $[\text{Cu}(\text{CO})(\eta\text{-C}_5\text{H}_5)]$ [5].



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-



*Crystal data for Va: $C_{32}H_{42}O_2CuRh_2$, $M = 731.0$, 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 $Fca2_1$ (No. 29), Mo- K_α X-radiation (graphite monochromator), $\lambda = 0.71069$ Å, $\mu(\text{Mo-}K_\alpha) = 17.3$ cm $^{-1}$. $R(R')$ 0.095 (0.079) for 1022 intensities with $I > 0.5\sigma(I)$.

*Crystal data for VI: $C_{31}H_{49}O_2P_2CuPtW$, $M = 954.1$, Monoclinic, $a = 10.516(5)$, $b = 17.898(8)$, $c = 18.134(6)$ Å, $\beta = 94.25(3)^\circ$, $Z = 4$, $D_c = 1.87$ g cm $^{-3}$, $U = 3403$ Å 3 , $F(000) = 1831$, space group $P2_1/c$ (No. 14), $\mu(\text{Mo-}K_\alpha) = 83.3$ cm $^{-1}$.

ment of the CuRh_2 ring (mean $\text{M}-\text{M}$ 2.56(1) Å), the pentahapto coordination of the $\eta\text{-C}_5\text{Me}_5$ 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 $\text{CuPtW}(\mu\text{-C})$ atoms adopt a "butterfly" configuration with the copper and platinum occupying the wing-tips (dihedral angle 89.7°). The $\text{Cu}-\text{Pt}$ 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 $\text{Pt}-\text{Pt}$ separation in species with structures IVb and IVc also correspond to little or no direct metal-metal bonding [8,12].

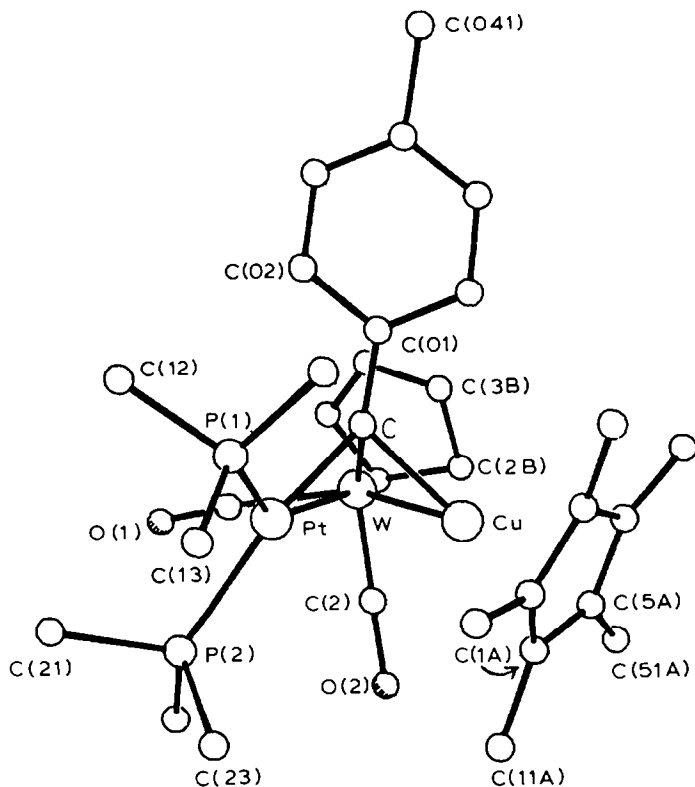


Fig. 1. The molecular structure of $[\text{CuPtW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\text{PMe}_3)_2(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_5\text{Me}_5)]$. Selected internuclear separations and angles: $\text{Cu}-\text{Pt}$, 2.807(3); $\text{Cu}-\text{W}$, 2.648(3); $\text{Pt}-\text{W}$, 2.779(1); $\text{C}-\text{Cu}$, 1.96(2); $\text{C}-\text{Pt}$, 2.00(2); $\text{C}-\text{W}$, 2.03(2); $\text{P}(1)-\text{Pt}$, 2.285(6); $\text{P}(2)-\text{Pt}$, 2.341(7) Å; angle $\text{W}-\text{C}(1)-\text{O}(1)$, 163° ; $\text{W}-\text{C}(2)-\text{O}(2)$, 171° .

From the results described herein, evidently I is a useful new reagent for organocopper chemistry, while an appreciation of the isolobal relationship between $\text{Cu}(\eta\text{-C}_5\text{Me}_5)$ 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 $-75^\circ C$ and then treated with $CuCl$ (0.34 g, 3.5 mmol) with stirring. The compound $[W\{=C(OMe)-C_6H_4Me-4\}(CO)_5]$ (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 $-50^\circ C$, 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 $2\theta \leq 50^\circ$ using the $\omega:2\theta$ scan technique. Of these reflections, 2245 (absorption corrected) had $I \geq 1\sigma(I)$. 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 $R = 0.055$ ($R' = 0.046$).

Acknowledgement. We thank the UK S.E.R.C. for support of this work.

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