and –365 ppm ($J_{P,P}$ = 178/178 Hz, respectively), which most probably corresponds to a second [(η^5-C_5HR_4)Cu] fragment coordinated to one of the phosphorus atoms of **4**. The signals at lower field are assigned to the two phosphorus atoms directly connected to the copper atom, whereas the high field signals originate from the remote pair of P atoms resembling P_4 more closely. Since coordination of the extra copper fragment affects the high field signal and leaves the lower field signal almost unchanged, the coordination must take place at one of the more remote pair of P atoms as shown in scheme 1. A comparison of ^{31}P NMR data of **4** (for **5** the same argument applies) with those of [($Ph_3P)_2RhCl(\eta^2$-$P_4)$] (**6**) ($\delta(P_A)$ = –279.4, $\delta(P_B)$ = –284.0) [4] and [(C_5Me_5)Co(CO)-(η^2-P_4)] (**7**) ($\delta(P_A)$ = –258.2 (t), $\delta(P_X)$ = –335.9 (q), $\delta(P_Y)$ = –376.9 (q) [5]) strongly supports an interpretation of the P_4 ligand in **4** (and **5**) as edge-opened P_4^{2-} resulting from oxidative addition of P_4 to the tetraisopropylcyclopentadienyl copper fragment as shown in scheme 1.

The rhodium complex **6** with its side-on coordination of one P–P bond to the central atom exhibits a distorted, but intact tetrahedron with a very small chemical shift difference $\Delta\delta$ between P_A and P_B of less than 5 ppm.

The average chemical shift of the P_4 ligand of cobalt complex **7** is –310 ppm and the chemical shift difference $\Delta\delta$ between P_A and P_X/P_Y is about 120 ppm.

The average chemical shift of –241 ppm is lower in field than the values observed for **6** or **7** and the chemical shift difference $\Delta\delta$ of 214 ppm observed for the novel copper complex **4** is even larger than that observed for the P_4^{2-} ligand in complex **7**. Therefore, **4** and **5** have to be interpreted as Cu(III) complexes resulting from oxidative addition of P_4 to the tetraisopropylcyclopentadienylcopper fragment.

Experimental Part

Carbonyl(tetraisopropylcyclopentadienyl)copper(I) (**3**): To a magnetically stirred suspension of 0.87 g (8.87 mmol) of finely ground cuprous chloride in 100 ml of freshly distilled THF a solution of 2.35 g (9.1 mmol) of sodium tetraisopropylcyclopentadienide was added dropwise. The reaction mixture was stirred at –78 °C for 90 min with formation of a dark green solution. Then carbon monoxide was admitted to the flask and the mixture was allowed to thaw to room temperature. The dark brown solution was subjected to centrifugation to remove unsoluble material, then evaporated to give dark brown, oily product.

C, H analysis for $C_{18}H_{29}CuO$, calculated: C 65,91, H 9.37, found: C 66.70, H 8.95%.

^{1}H NMR (toluene-d_8, 400 MHz, 25 °C): δ = 5.72 (s, ring-H), 3.23 (sep, 2 H, CHMe$_2$) 3.09 (sep, 2 H, CHMe$_2$), 1.55 (d, 6 H, CH_3, $^3J_{H,H}$ = 7.2 Hz), 1.54 (d, 6 H, CH_3, $^3J_{H,H}$ = 7.2 Hz), 1.45 (d, 6 H, CH_3, $^3J_{H,H}$ = 6.8 Hz), 1,37 (d, 6 H, CH_3, $^3J_{H,H}$ = 6.8 Hz). – ^{13}C{^{1}H} NMR (toluene-d_8, 400 MHz, –30 °C): δ = 188 (1 C, CuCO), 122 (2 C, CCHMe$_2$), 120 (2 C, CCHMe$_2$), 89 (2 C, ring CH), alkyl signals could not be assigned, because they are broad and superimposed. – EI-MS, 70 eV, *m/e* (%): 324 (M^+, 50), 296 (M^+–CO, 67), 281 (M^+–CO–CHMe$_2$, 34), 107 ($C_8H_{11}^+$, 100). – IR (toluene, 25 °C) ν_{CO} = 2062 cm^{-1}.

Complexes **4** and **5**: From 0.9 g (9.1 mmol) of CuCl and 2.35 g (9.1 mmol) of sodium tetraisopropylcyclopentadienide brown, oily **3** was obtained as stated before and dissolved in 50 ml of toluene. 0.26 g (2.1 mmol) of P_4 was added and the solution was heated to reflux for ca. 5 min, until the CO absorption had completely disappeared in IR spectra of the reaction solution. The solvent was removed in vacuo and the dark green residue was extracted with petroleum ether. After centrifugation the clear solution was removed in vacuo and the residue was warmed to 50–55 °C for 6 h in vacuo to remove all volatiles including small amounts of tetraisopropylcyclopentadiene. 100–150 mg portions of the remainder were dissolved in petroleum ether, mixed with 2 g of silylated silica gel, evaporated until the mixture was flowing freely. The mixture was put on top of a column (35×2 cm) loaded with silica gel in petroleum ether at a temperature of –20 °C. Elution with petroleum ether/toluene 50:1 a bright green fraction containing both **4** and **5** was eluted. The total amount of **4** and **5** in the solid residue after solvent evaporation was approximately 1 g, the molar ratio of **4** and **5** was about 1:1 according to ^{31}P NMR spectra.

4: ^{31}P NMR (C_6D_6, 400 MHz, 25 °C, 85% H_3PO_4 as external standard): δ = –134 (t, 2 P, $^1J_{P,P}$ = 178 Hz), –348 (t, 2 P, $^1J_{P,P}$ = 178 Hz).

5: ^{31}P NMR (C_6D_6, 400 MHz, 25 °C, 85% H_3PO_4 as external standard): δ = –141 ("t", 2 P, $^1J_{P,P}$ = 178 Hz), –311 ("q", 1 P, $^1J_{P,P}$ = 178 Hz), –365 ("q", 1 P, $^1J_{P,P}$ = 178 Hz).

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