4H; CH_2), 1.41 (dt, $^3J(H,P) = 22.70$ Hz; $^3J(H,H) = 7.33$ Hz; 6H; CH_3); ^{13}C NMR (100.5 MHz, CD_3NO_2, CF_3COOD, 23 °C, TMS): $\delta = 150.14$ (dm, $^1J(C,F) = -265.7$ Hz; C2/C3/C5/C6, benzene), 137.83 (d, $^4J(C,P) = 3.6$ Hz; C4, phenyl), 134.82 (d, $^2J(C,P) = 11.1$ Hz; C2/C6, phenyl), 132.14 (d, $^3J(C,P) = 12.9$ Hz; C3/C5, phenyl), 121.71 (q, $^1J(C,F) = -318.0$ Hz; CF_3), 115.80 (d, $^1J(C,P) = 88.3$ Hz; C1, phenyl), 110.65 (dm, $^1J(C,P) = 88.3$ Hz; C1/C4, benzene), 19.36 (d, $^1J(C,P) = 49.7$ Hz; CH_2), 6.94 (d, $^2J(C,P) = 5.5$ Hz; CH_3); ^{31}P NMR (161.7 MHz, CD_3NO_2, CF_3COOD, 23 °C, ext. H_3PO_4): $\delta = 26.71$ (s).

6: Compound **3** (0.80 mL, 4.43 mmol) and **6** (0.605 g, 4.95 mmol) were added to a solution of **5** (0.149 g, 0.55 mmol) in chlorobenzene (20 mL) and the solution was stirred under reflux. After 12 h the yellow precipitate was filtered off, washed with CH_2Cl_2 (4 × 5 mL) and dried for 12 h under high vacuum. Yield: 1.24 g (98%); ^1H NMR (400.05 MHz, CD_3CN, 24 °C, TMS): $\delta = 8.05$ (d, $^3J(H,H) = 7.57$ Hz, 8H; H-2/H-6), 7.83 (d, $^3J(H,H) = 7.57$ Hz, 8H; H-2/H-6), 6.87 (d, $^3J(H,H) = 7.57$ Hz, 8H; H-3/H-5), 6.86 (d, $^3J(H,H) = 7.57$ Hz, 8H; H-3/H-5), 3.24 (s, 24H; CH_3), 3.20 (s, 24H; CH_3); ^{13}C NMR (100.5 MHz, CD_3CN, 24 °C, TMS): $\delta = 157.30$ (s; C4, DMAP), 156.81 (s; C4, DMAP), 142.29 (s; C2/C6, DMAP), 140.42 (s; C2/C6, DMAP), 140.37 (s; C1/C4/C5/C8, naphthalene), 138.49 (s; C2/C3/C6/C7, naphthalene), 131.34 (s; C9/C10, naphthalene), 121.88 (q, $^1J(C,F) = -319.9$ Hz; CF_3), 110.86 (s; C3/C5, DMAP), 110.70 (s; C3/C5, DMAP), 41.80 (s; CH_3), 41.60 (s; CH_3); ^{19}F NMR (470.4 MHz, CD_3CN, 20 °C, C_6F_6): $\delta = -77.9$ (s; CF_3).

7a,b: Compound **3** (2 mmol) and PEt_2Ph or $PEtPh_2$ (2 mmol) were added to a solution of **5** (0.5 mmol) in chlorobenzene (20 mL) and the solution was stirred under reflux. After 48 h the suspension was cooled to −20 °C, the precipitation was completed by the addition of Et_2O (20 mL), and the precipitate was filtered off, washed with Et_2O (5 × 5 mL), and dried for 12 h under high vacuum.

7a: pale yellow powder; yield: 95%; ^1H NMR (400.05 MHz, CD_3CN, 24 °C, TMS): $\delta = 7.85$ (m, 8H; H-2/H-6, phenyl), 7.73 (m, 4H; H-4, phenyl), 7.67 (m, 8H; H-3/H-5, phenyl), 2.85 (m, 16H; CH_2), 1.06 (dt, $^3J(H,P) = 21.73$ Hz, $^3J(H,H) = 7.57$ Hz, 12H; CH_3), 1.01 (dt, $^3J(H,P) = 22.22$ Hz, $^3J(H,H) = 7.32$ Hz, 12H; CH_3); ^{13}C NMR (100.5 MHz, CD_3CN, 24 °C, TMS): $\delta = 167.65$ (dd, $^1J(C,F) = -262.9$ Hz, $^2J(C,F) = 10.1$ Hz; C4/C8, naphthalene), 166.26 (dm, $^1J(C,F) = -270.3$ Hz; C2/C6, naphthalene), 136.82 (d, $^4J(C,P) = 3.7$ Hz; C4, phenyl), 135.99 (s; C4, phenyl), 133.39 (d, $^2J(C,P) = 11.0$ Hz; C2/C6, phenyl), 132.27 (d, $^2J(C,P) = 9.2$ Hz; C2/C6, phenyl), 131.63 (d, $^3J(C,P) = 12.8$ Hz; C3/C5, phenyl), 131.46 (d, $^3J(C,P) = 12.9$ Hz; C3/C5, phenyl), 129.88 (m; C9/C10, naphthalene), 121.92 (q, $^1J(C,F) = -319.9$ Hz; CF_3), 120.01 (d, $^1J(C,P) = 86.4$ Hz; C1, phenyl), 116.31 (d, $^1J(C,P) = 84.6$ Hz; C1, phenyl), 106.46 (m; C3/C7, naphthalene), 102.26 (dd, $^1J(C,P) = 75.3$ Hz, $^2J(C,F) = 19.4$ Hz; C1/C5, naphthalene), 17.78 (d, $^1J(C,P) = 44.1$ Hz; CH_2), 15.40 (d, $^1J(C,P) = 47.8$ Hz; CH_2), 6.64 (d, $^2J(C,P) = 3.7$ Hz; CH_3), 6.11 (d, $^2J(C,P) = 5.5$ Hz; CH_3); ^{19}F NMR (470.4 MHz, CD_3CN, 20 °C, C_6F_6): $\delta = -78.0$ (s, 12F; CF_3), −74.8 (m, 2F; F-4/F-8), −67.9 (m, 2F; F-2/F-6); ^{31}P NMR (161.7 MHz, CD_3CN, 20 °C, ext. H_3PO_4): $\delta = 42.98$ (dd, $^3J(P,F) = 18.4$ Hz; $^3J(P,F) = 8.2$ Hz; P-3/P-7), 35.71 (d, $^3J(P,F) = 6.2$ Hz; P-1/P-5).

7b: pale orange powder; yield: 88%; ^1H NMR (400.05 MHz, CD_3CN, 21 °C, TMS): $\delta = 7.85$–7.62 (m, 40H; phenyl), 3.33 (m, 8H; CH_2), 1.11 (m, 12H; CH_3); ^{13}C NMR (100.5 MHz, CD_3CN, 21 °C, TMS): $\delta = 137.19$ (s; C4, phenyl), 136.69 (s; C4, phenyl), 133.34 (d, $^2J(C,P) = 11.0$ Hz; C2/C6, phenyl), 132.55 (d, $^2J(C,P) = 11.1$ Hz; C2/C6, phenyl), 131.66 (d, $^3J(C,P) = 14.7$ Hz; C3/C5, phenyl), 130.70 (d, $^3J(C,P) = 12.9$ Hz; C3/C5, phenyl), 129.66 (m; C9/C10, naphthalene), 121.92 (q, $^1J(C,F) = -319.9$ Hz; CF_3), 119.10 (d, $^1J(C,P) = 86.4$ Hz; C1, phenyl), 115.57 (d, $^1J(C,P) = 84.6$ Hz; C1, phenyl), 103.72 (m; C3/C7, naphthalene), 101.18 (m; C1/C5, naphthalene), 18.53 (d, $^1J(C,P) = 51.5$ Hz; CH_2), 17.44 (d, $^1J(C,P) = 53.3$ Hz; CH_2), 8.21 (d, $^2J(C,P) = 5.5$ Hz; CH_3), 7.09 (d, $^2J(C,P) = 3.7$ Hz; CH_3); ^{19}F NMR (470.4 MHz, CD_3CN, 20 °C, C_6F_6): $\delta = -78.0$ (s, 12F; CF_3), −69.0 (m, 2F; F-4/F-8), −66.6 (m, 2F; F-2/F-6); ^{31}P NMR (161.7 MHz, CD_3CN, 20 °C, ext. H_3PO_4): $\delta = 32.63$ (d, $^3J(P,F) = 18.2$ Hz; P-3/P-7), 26.07 (d, $^3J(P,F) = 4.1$ Hz; P-1/P-5).

9a: Compound **9** (1 mmol) was suspended in CH_2Cl_2 (30 mL) and **3** (4 mmol) was added. Subsequently, PEt_3 (4 mmol) dissolved in CH_2Cl_2 (10 mL) was added to the mixture. After the mixture had been stirred for 12 h at room temperature, the pale green precipitate was filtered off, washed with CH_2Cl_2 (3 × 5 mL) and dried for 12 h under high vacuum. Yield: 62%; ^1H NMR (399.65 MHz, CD_3CN, 20 °C, TMS): 2.85 (m, 24H; CH_2) 1.29 (m, 36H; CH_3).

10: Compound **9** (1 mmol) was suspended in CH_2Cl_2 (20 mL) and **3** (4 mmol) was added. Subsequently PPh_3 (6 mmol) dissolved in CH_2Cl_2 (20 mL) was added to the mixture. After the mixture had been stirred for 12 h at room temperature Et_2O (100 mL) was added to precipitate a green solid. The solid was filtered off, washed with Et_2O (3 × 5 mL) and dried for 12 h under vacuum. Yield: 69%; UV/Vis (CH_3CN): λ_{max} (ε) = 668 (4870), 614 (5355), %72 (2920), 439 (6330), 382 (8520), 270 (37085), 214 (91945).

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A New Mode of Reaction of *tert*-Butylphosphaethyne: Trinuclear Cyclopentadienylcobalt Clusters with P, PS, and PO as μ_3 Complex Ligands**

Jan Foerstner, Falk Olbrich, and Holger Butenschön*

Dedicated to Professor Erwin Weiss on the occasion of his 70th birthday

"Phosphaalkynes correspond to alkynes in all aspects, to nitriles in nothing." This remark by Regitz[1] is substantiated by the results of our investigations of the chemistry of [ω-phosphanyl(ethylcyclopentadienyl)]cobalt complexes. Herein we report on reactions of such complexes with *tert*-butylphosphaethyne that in addition to diphosphete complexes result in the formation of μ_3-phosphido clusters in good yields. The "naked" phosphorus ligand in these clusters can be oxidized with elemental sulfur or with oxygen in the air to give PS and PO ligands, respectively.

The chemistry of phosphaethynes has been investigated intensely in the past few years.[2] In a few cases mononuclear transition metal complexes with a monomeric phosphaethyne ligand have been prepared.[3–5] Because we were able to coordinate alkynes with the [(ω-di-*tert*-butylphosphanyl)ethylcyclopentadienyl]cobalt (Cp'Co) fragment without di- or trimerization,[6, 7] we investigated reactions of Cp'Co complexes with *tert*-butylphosphaethyne. The paramagnetic chloride **1** and the

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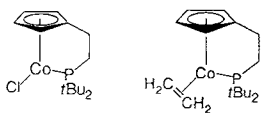
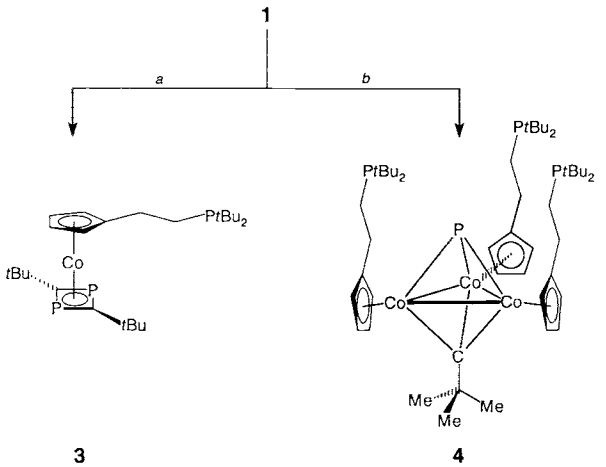


1 2

ethene complex **2** generated from **1** proved to be good starting materials for Cp'Co complexes: they were applied either in the presence of sodium/amalgam (**1**) or directly (**2**) with a new ligand. The reaction starting with **1** avoids the detour via the ethene complex **2** and usually results in higher yields. Compound **2** should be used as starting material in reactions with ligands (for example arenes) that can undergo side reactions with sodium amalgam.[7]

Treatment of **1** in the presence of sodium amalgam at $-50\,^{\circ}C$ with a threefold molar excess of *tert*-butylphosphaethyne, followed by allowing the mixture to warm up to $-30\,^{\circ}C$ gives the diphosphete complex **3**, in which the "phosphane arm" has been decomplexed, in 71% yield (Scheme 1). A compound analagous



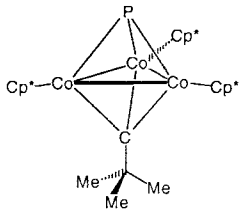
3 4

Scheme 1. a) 3 equiv PC*t*Bu, Na/Hg, THF, $-50 \rightarrow -30\,^{\circ}C$, 4 h, 71%; b) 0.33 equiv PC*t*Bu, Na/Hg, THF, $-50 \rightarrow 20\,^{\circ}C$, 90 min, 85%.

to **3** is obtained by the reaction of cyclopentadienyldi(ethene)cobalt(I) with *tert*-butylphosphaethyne.[8, 9] However, treatment of *tert*-butylphosphaethyne with a threefold excess of **1** at 20 °C leads unexpectedly to the μ_3-carbyne-μ_3-phosphidotricobalt cluster **4** as the sole product in 85% yield. Treatment of **2** with an equimolar amount of *tert*-butylphosphaethyne results in the diphosphete complex **3** (50% yield) together with cluster **4** (5% yield). Such a mode of reaction of *tert*-butylphosphaethyne, which is characterized by a complete breakage of the phosphorus–carbon triple bond and coordination of the phosphorus atom and the carbyne fragment on opposite faces of the tricobalt plane, was hitherto unkown. The quotation of Regitz mentioned at the beginning is confirmed impressively, however, because such reactions of alkynes have been observed at high temperatures (195 °C) and lead to biscarbyne clusters.[10–12] Zenneck et al.[13] and Stone et al.[14] have described compounds that result from cleavage of the P–C bond of *tert*-butylphosphaethyne and subsequent reformation of new P–C bonds.

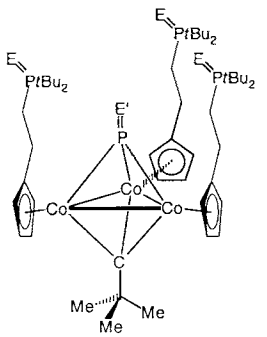
The question of how important is it to start from cyclopentadienylcobalt complexes like **1** or **2** with a phosphanylalkyl substituent for the formation of clusters like **4** was studied by treating common cyclopentadienyl- and pentamethylcyclopentadienylcobalt compounds with *tert*-butylphosphaethyne. The reaction of cyclopentadienyldi(ethene)cobalt with *tert*-butylphosphaethyne for 3 h at 20 °C, followed by evaporation of the solvent, and heating up to 180 °C for 5 min gave no evidence for the formation of a cluster corresponding to **4**.

Treatment of a 1.5 molar excess of $[\{Cp^*CoCl\}_2]$,[15] the dimer corresponding to **1** with pentamethylcyclopentadienyl (Cp*) ligands instead of the Cp' ligand, under the conditions chosen for **1** resulted in a mixture of the diphosphete complex[16] and traces of cluster **5** corresponding to **4** in an overall yield of 57%. When the reaction mixture was heated to 180 °C, **5** was obtained as the only isolated product in 1-2% yield. Thus, the "phosphane arm" promotes the formation of **4** extraordinarily. Possibly in the reaction sequence leading to **4**, initially the originally desired complex with *tert*-butylphosphaethyne is formed, which then reacts further with excess **1** leading to the formation of the tricobalt cluster. Compound **3** does not react with **1** to give **4**, and therefore it is not regarded as an intermediate in the formation of **4**. To date there are only a few μ_3-phosphido clusters known; these have been generated by treatment of phosphorus(III) halides or even P_4 with low-valent transition metal complexes.[17–21]



5 $Cp^* = C_5Me_5$

Preliminary studies on the reactivity were performed by treating the cluster **4** with elemental sulfur. Within 20 min **4** reacts with S_8 in diethyl ether at 20 °C to give the air-stable sulfuration product **6** in 77% yield, in which all four phosphorus atoms have been oxidized (Scheme 2). Compound **6** is one of the very rare complexes with PS as a ligand.[22, 23] In addition to the main product **6**, the phosphorus monoxide complex **7** was separated by column chromatography in low but reproducible yield (1–2%). It is probably generated from incompletely sulfurated product on the chromatography phase silica gel and adsorbed oxygen. This suggests that **4** is initially sulfurated at the phosphorus atoms of the phosphane fragments and then at the phosphido ligand. Oxidation of **4** with oxygen in air leads to the cluster **8**, which is oxidized at all four phosphorus atoms, in good yield (68%). This was characterized by mass spectrometry but decomposes very fast. Compounds **7** and **8** are examples of a rare class of complexes with PO as ligand, first discovered by Scherer et al., which otherwise were only found in interstellar space or as short-lived extremely reactive species.[24–26] The new compounds were characterized by spectroscopy and mass spectrometry (Table 1), and the structure of the PO complex **7** was determined by X-ray structure analysis (Fig. 1).[33]



6: E = E' = S
7: E = S, E' = O
8: E = E' = O

6 + **7** $\xleftarrow{a}$ **4** $\xrightarrow{b}$ **8**

Scheme 2. a) 1. S_8, Et_2O, 20 °C, 20 min; 2. column chromatography on silica gel (petroleum ether/diethyl ether 6:1, red fraction), **6** (77%), elution with diethyl ether (orange fraction) **7** (1–2%). b) 1. Air oxygen, diethyl ether; 2. column chromatography on silica gel, ethyl acetate/ethanol 1:1, red fraction) **8** (68%).

The structure of **7** in the crystal shows a distorted, nearly C_3 symmetrical trigonal bipyramid in which three cobalt atoms Co1, Co2, and Co3 form the base. The phosphorus atom P4 of the PO ligand is located nearly perpendicular above the center of this plane, below which the carbon atom C16 of the *tert*-butylcarbyne ligand is located. The axis comprising the atoms O, P4, C16, and C17 is almost linear (angle O-P4-C16 179.3°,

Table 1. Selected spectroscopic data of new compounds (+ and − denote the positive (C, CH_2) and negative phase (CH, CH_3), respectively, in APT ^{13}C NMR spectra). All compounds gave satisfactory elemental analyses or high-resolution mass spectra.

3: ^1H NMR (200 MHz, C_6D_6): $\delta = 1.04$ (s, 18H), 1.27 (d, 18H, $^3J(P,H) = 11$ Hz), 2.08 (dt, 2H, $^3J(P,H) = 11$ Hz, $^3J(H,H) = 6$ Hz), 3.08 (m, 2H, $^2J(P,H) = 13$ Hz, $^3J(H,H) = 6$ Hz), 4.8 (m, 2H, $\Sigma J = 4$ Hz), 5.23 (m, 2H). ^{13}C NMR (50 MHz, C_6D_6): $\delta = 23.7$ (+, d, PCH_2CH_2, $^2J(P,C) = 22$ Hz), 30.3 (−, $PCCH_3$, $^2J(P,C) = 13.8$ Hz), 31.5 (−, t, P_2CCCH_3, $^3J(P,C) = 4.6$ Hz), 31.6 (+, d, $PCCH_3$, $^1J(P,C) = 23$ Hz), 34.5 (+, t, P_2CCCH_3, $^2J(P,C) = 6.9$ Hz), 40.6 (+, d, PCH_2CH_2, $^1J(P,C) = 17.6$ Hz), 79.5 (−, cyclopentadienyl-CH), 81.1 (−, cyclopentadienyl-CH), 105.6 (+, d, cyclopentadienyl-CCH_2, $J(C,P) = 14$ Hz), 108.5 (+, t, $^1J(P,C) = 54.3$ Hz). ^{31}P NMR (81 MHz, C_6D_6, ext. standard H_3PO_4): $\delta = 37.8$ (P_2CCCH_3), 28.9 ($PCCH_3$). MS (70 eV): m/z: 496 (M^+, 3%).

4: ^1H NMR (400 MHz, C_6D_6): $\delta = 1.20$ (d, 54H, $PCCH_3$, $^3J(P,H) = 10.7$ Hz), 1.70 (m, 2H, PCH_2CH_2), 2.39 (m, 2H, PCH_2, $^2J(P,H) = 8.3$ Hz), 2.45 (s, 9H, Co_3CCCH_3), 4.42 (AA'BB', 2H, cyclopentadienyl-H, $\Sigma J = 4$ Hz), 4.96 (AA'BB', 2H, cyclopentadienyl-H). ^{13}C NMR (100 MHz, C_6D_6): $\delta = 24.2$ (+, d, CH_2), 24.3 (+, d, CH_2), 29.9 (−, d, $PCCH_3$, $^2J(P,C) = 13.5$ Hz), 31.4 (+, d, $PCCH_3$, $^1J(P,C) = 24.5$ Hz), 37.3 (−, Co_3CCCH_3), 59.9 (+, Co_3CCCH_3), 67.9 (+, d, Co_3CCCH_3, $^2J(P,C) = 10.1$ Hz), 81.0 (−, cyclopentadienyl-CH), 81.9 (−, d, cyclopentadienyl-CH, $J(P,C) = 1.9$ Hz), 103.8 (+, d, cyclopentadienyl-CCH_2, $J(P,C) = 15.2$ Hz). ^{31}P NMR (162 MHz, C_6D_6, ext. standard H_3PO_4): $\delta = 27.0$ (s), 189.9 (br. s). MS (CI - methane): m/z: 989.9 (M^+, 10%).

5: ^1H NMR (200 MHz, CD_2Cl_2): $\delta = 1.63$ (s, 45H), 2.29 (s, 9H). MS (70 eV): m/z: 682 (M^+, 100%).

6: IR (KBr): $\tilde{\nu}$[cm^{-1}] = 2963, 1262, 1099, 1025, 804, 735 (PS), 650 (CCo_3). ^1H NMR (200 MHz, $CDCl_3$): $\delta = 1.33$ (d, 54H, $PCCH_3$, $^3J(P,H) = 15$ Hz), 2.06 (m, 6H, PCH_2CH_2), 2.28 (m, 6H, PCH_2), 2.33 (s, 9H, Co_3CCCH_3), 4.5 (m, 6H, cyclopentadienyl-H), 4.72 (m, 6H, cyclopentadienyl-H). ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 23.8$ (+, d, PCH_2CH_2, $^2J(P,C) = 13.6$ Hz), 24.2 (+, d, PCH_2, $^1J(P,C) = 26.2$ Hz), 27.6 (−, $PCCH_3$), 37.8 (+, d, $PCCH_3$, $^1J(P,C) = 41.6$ Hz), 62.2 (+, Co_3CCCH_3), 65.8 (+, Co_3CCCH_3), 82.5 (−, cyclopentadienyl-CH), 86.3 (−, cyclopentadienyl-CH), 102.4 (+, d, cyclopentadienyl-CCH_2, $J(P,C) = 15.4$ Hz). ^{31}P NMR (81 MHz, $CDCl_3$, ext. standard H_3PO_4): $\delta = 78.5$ [$C(tBu_3)_2P{=}S$], 578 ($Co_3P{=}S$). MS [FAB (*ortho*-nitrobenzyl)alcohol]: $m/z = 1117$ ($M^+ + 1$, 15%).

7: IR ($CHCl_3$): $\tilde{\nu}$[cm^{-1}] = 2964, 2928, 1604, 1260, 1228, 1132. ^1H NMR (200 MHz, $CDCl_3$): $\delta = 1.35$ (d, 54H, $PCCH_3$, $^3J(P,H) = 15$ Hz), 2.07 (m, 6H, PCH_2CH_2), 2.22 (m, 6H, PCH_2), 2.31 (s, 9H, Co_3CCCH_3), 4.53 (m, 6H, cyclopentadienyl-CH), 4.98 (m, 6H, cyclopentadienyl-CH). ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 25.1$ (+, d, PCH_2CH_2 or PCH_2CH_2, $J(P,C) = 20$ Hz), 27.6 (−, $PCCH_3$), 37.6 (−, Co_3CCCH_3), 37.9 (+, d, $PCCH_3$), 62.5 (+, Co_3CC), 81.8 (−, cyclopentadienyl-CH), 84.4 (−, cyclopentadienyl-CH), 102.5 (+, d, cyclopentadienyl-CCH_2, $J(P,C) = 16.3$); signal for Co_3CC was not observed due to low sample concentration. MS (70 eV): m/z: 1100 (M^+, 100%).

8: MS (70 eV, 300 °C): $m/z = 1052$ (M^+, 18%), 1036 (21), 963 (37), 891 (17), 782 (18), 565 (21), 312 ($CoCp^*O$, 71).

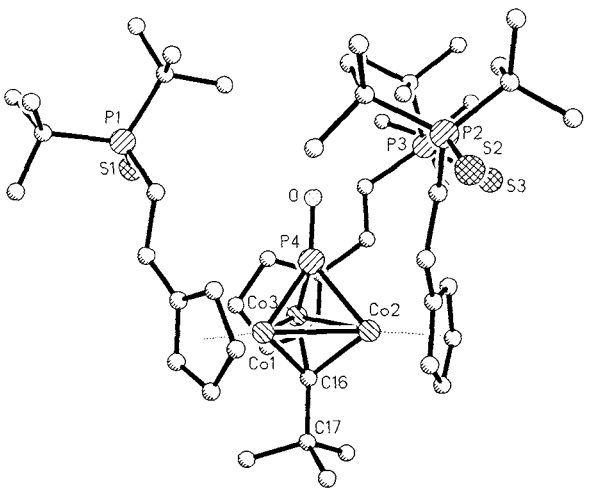


Fig. 1. Molecular structure of **7** in the crystal. Selected bond lengths [Å] and angles [°]: Co1–Co2 2.4751(8), Co2–Co3 2.4691(9), Co1–Co3 2.4592(8), Co1–P4 2.0959(13), Co2–P4 2.0964(13), Co3–P4 2.0941(13), P4–O 1.489(3), Co1–C16 1.885(4), Co2–C16 1.885(4), Co3–C16 1.890(5), Co–C(Cp) 2.070(5)–2.106(4), P–S 1.965(2); Co1-Co2-Co3 59.66(2), Co2-Co3-Co1 60.29(2), Co3-Co1-Co2 60.05(3), Co1-P4-Co2 72.37(4), Co2-P4-Co3 72.20(4), Co3-P4-Co1 71.88(4), Co1-C16-Co2 82.1(2), Co2-C16-Co3 81.7(2), Co3-C16-Co1 81.3(2), Co1-P4-O 137.4(2), Co2-P4-O 136.55(15), Co3-P4-O 137.5(2), Co1-C16-C17 130.4(3), Co2-C16-C17 130.6(3), Co3-C16-C17 131.8(3). Distance P4···C16 2.773(4) Å.

P4-C16-C17 179.2°). In the Co_3 plane the Co–Co distances range between 2.459–2.475 Å. The bond lengths Co–P4 are 2.095 Å, the bond lengths Co–C16 1.887 Å. The P4–O distance of 1.489 Å is nearly the same as that found by Scherer in the first P–O complex (1.46, 1.48 Å).[27] A substituted cyclopentadienyl ligand is attached to each Co atom at the periphery of the cluster with the coordinated carbon atoms at about the same distance from the cobalt atom (av Co–C(Cp) 2.084 Å). Remarkably, all three "phosphane arms" point in the direction of the face of the Co_3 plane to which the PO ligand is coordinated. The reason for this might be the steric hindrance of the *tert*-butylcarbyne ligand at the opposite face. An attractive interaction from the O atom to the atoms P1, P2, or P3 was not observed (the shortest distance is 4.643 Å for O···P1).

We have discovered a hitherto unkown mode of reactivity of *tert*-butylphosphaethyne, which in analogy to the reaction of alkynes with cyclopentadienylcobalt complexes leads to μ_3-carbyne-μ_3-phosphidotricobalt clusters with the [ω-phosphanyl-(ethylcyclopentadienyl)]cobalt complexes **1** and **2**, whose phosphido ligand can be oxidized to PS and PO ligands, respectively. The "phosphane arm" in **1** and **2** is evidently needed for the formation of the cluster, since comparable cyclopentadienyl or pentamethylcyclopentadienyl metal complexes form analogous clusters at best in traces. We are currently investigating the role of the "phosphane arm" in the formation of **4**.

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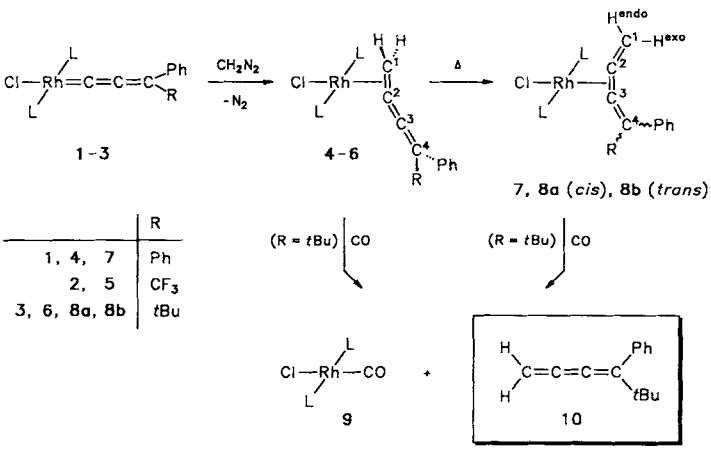
[27] X-ray crystal structure analysis of **7**: DIP2020 Image Plate from Enraf-Nonius, $Mo_{K\alpha}$ radiation, graphite monochromator. Structure resolution was performed with direct methods (SHELXS-86), refinement with full-matrix least-squares refinement at F^2 (SHELXL-93). $C_{50}H_{87}Co_3OP_4S_3$, $M_r = 1101.05$, orthorhombic, space group $Pna2_1$, $Z = 4$, $a = 23.446(3)$ $b = 22.794(2)$ $c = 10.531(2)$ Å, $V = 5628.1(14)$ Å^3, $\rho_{calcd} = 1.30$ g cm^{-3}, $\mu = 1.13$ mm^{-1}, 34477 measured reflections, 8159 independent, and 7446 observed reflections for $I > 2\sigma(I)$, temperature 20 °C. All non-hydrogen atoms were refined anisotropically, H atoms calculated for idealized positions. $R_1 = 0.0375$, $wR_2 = 0.0859$ (all data) for 569 parameters and 1 restraint. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-404656.



Scheme 1. L = P*i*Pr$_3$.

Methyl Iodide as a Source of CH_2: Two Routes for Generating 1,1-Disubstituted Butatrienes in the Coordination Sphere of a Transition Metal**

Helmut Werner,* Matthias Laubender, Ralf Wiedemann, and Bettina Windmüller

Dedicated to Professor Max Herberhold on the occasion of his 60th birthday

Following the reports on the synthesis of vinylidene complexes of the general type *trans*-[RhCl(=C=CHR)(P*i*Pr$_3$)$_2$],[1] we recently also described an efficient preparative route to the corresponding allenylidene compounds *trans*-[RhCl(=C=C=CRR')(P*i*Pr$_3$)$_2$].[2] In the course of investigations into the reactivity of these compounds, we have now discovered that the allenylidene unit can be converted by two different pathways into 1,1-disubstituted butatrienes $H_2C{=}C{=}C{=}CRR'$, which because of their lability are otherwise hardly accessible. We note that up to now there is no precedent for the coupling of a CH_2 fragment, generated from CH_2N_2 or CH_3I, with an allenylidene moiety to yield a butatriene. Moreover, allenes can likewise be obtained from allenylidenerhodium complexes.

In contrast to compounds *trans*-[RhCl(=C=CHR)(P*i*Pr$_3$)$_2$] (R = Ph, *t*Bu, CO_2Me), which are inert in the presence of CH_2N_2,[3] complexes **1**–**3**[4] react with excess diazomethane at room temperature within a few minutes.[5] The red or orange butatriene complexes **4**–**6** (Scheme 1), which are only moderately sensitive to air and water, were isolated in nearly quantitative yield. The compositions of **4**–**6** have been confirmed by elemental analysis. The proposed structure shown in Scheme 1 is particularly supported by the ^{13}C NMR spectra (Table 1), which display four signals between $\delta = 180$ and 12 for the carbon atoms of the butatriene ligand. Two of these signals show a relatively large Rh–C coupling and are thus assigned to the C atoms of the butatriene ligand bonded to the metal. The chemical shift of the C^1 resonance as well as the ^1J(CH) coupling constant (161.4 Hz) of **4** indicate a predominant sp^3 character of this carbon atom which implies that the bonding between Rh, C^1, and C^2 is related to that of a metallacyclopropane.

The X-ray crystal structure analysis of **4** (Fig. 1)[6] reveals a distorted square-planar coordination around the central atom;

Table 1. Selected spectroscopic data of complexes **4**–**8** and **12**–**14**, and of the cumulenes **10** and **16** (without data for phosphane ligands, phenyl and *tert*-butyl groups); for assignment C^1–C^4 and H^{exo}, H^{endo} see Scheme 1.

4: ^{1}H NMR (400 MHz, C_6D_6): $\delta = 2.61$ [dvt, $N = 10.8$, J(H,H) = 1.6 Hz, CH_2]; ^{13}C NMR (100.6 MHz, C_6D_6): $\delta = 181.50$ (s, C=CPh$_2$), 111.39 (s, CPh$_2$), 108.51 [dt, J(Rh,C) = 22.1, J(P,C) = 8.0 Hz, C=CH$_2$], 13.03 [d, J(Rh,C) = 13.6 Hz, CH$_2$]

5: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.87$ and 2.78 [each dddd, J(Rh,H) = 6.0, J(P^1,H) = 5.6, J(P^2,H) = 5.6, J(H,H) = 1.6 Hz, 1H each of CH$_2$]; ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 183.83$ [s, C=C(Ph)CF$_3$], 125.02 [q, J(F,C) = 272.2 Hz, CF$_3$], 109.86 [dt, J(Rh,C) = 22.1, J(P,C) = 4.0 Hz, C=CH$_2$], 99.34 [q, J(F,C) = 34.0 Hz, C(Ph)CF$_3$], 16.12 [d, J(Rh,C) = 14.7 Hz, CH$_2$]; ^{19}F NMR (376.5 MHz, $CDCl_3$): $\delta = -58.60$ (s)

6: ^{13}C NMR (100.6 MHz, C_6D_6): $\delta = 179.30$ [s, C=C(Ph)*t*Bu], 100.17 [s, C(Ph)*t*Bu], 109.40 [dt, J(Rh,C) = 23.1, J(P,C) = 5.0 Hz, C=CH$_2$], 12.52 [d, J(Rh,C) = 13.4 Hz, CH$_2$]

7: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 5.46$ and 5.00 (each s, br, 1H each of CH$_2$); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 142.69$ [dt, J(Rh,C) = 17.1, J(P,C) = 4.0 Hz, C^2/C^3], 137.96 [dt, J(Rh,C) = 20.1, J(P,C) = 5.0 Hz, C^2/C^3], 127.59 (s, br, CPh$_2$), 98.36 (s, br, CH$_2$)

8a: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 5.62$ [t, J(P,H) = 2.4 Hz, 1H of CH$_2$], 5.21 (s, br, 1H of CH$_2$); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 143.57$ [dt, J(Rh,C) = 16.1, J(P,C) = 4.0 Hz, C^2/C^3], 134.27 [s, C(Ph)*t*Bu], 132.59 [dt, J(Rh,C) = 18.1, J(P,C) = 4.0 Hz, C^2/C^3], 100.20 (s, CH$_2$); ^{31}P NMR (162.0 MHz, $CDCl_3$): $\delta = 28.05$ [d, J(Rh,P) = 119.2 Hz]

8b: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.65$ and 4.19 (each s, br, 1H each of CH$_2$); ^{31}P NMR (162.0 MHz, $CDCl_3$): $\delta = 28.99$ [d, J(Rh,P) = 119.5 Hz]

10: IR (C_6H_6): $\tilde{\nu}$ [cm^{-1}] = 2050 (C=C=C); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 5.13$ and 5.05 [each d, J(H,H) = 7.6 Hz, 1H each of CH$_2$]; ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 168.64$ and 158.69 (each s, =C=), 135.27 (s, CPh$_2$), 89.31 (s, CH$_2$)

12: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 5.13$ and 4.78 (each s, 1H each of CH$_2$); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 142.43$ [dt, J(Rh,C) = 18.1, J(P,C) = 3.0 Hz, C^2/C^3], 135.87 [dt, J(Rh,C) = 20.1, J(P,C) = 5.0 Hz, C^2/C^3], 127.49 (s, br, CPh$_2$), 98.31 (s, CH$_2$)

13: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.41$ [dt, J(Rh,H) = 2.1, J(P,H) = 5.1 Hz, CH$_2$]; ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 173.34$ [dt, J(Rh,C) = 23.1, J(P,C) = 6.0 Hz, =C=], 123.10 (s, CPh$_2$), 16.40 [d, J(Rh,C) = 13.1 Hz, CH$_2$]

14: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.62$ (m, CH$_2$); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 179.00$ (m, =C=), 122.47 [q, J(F,C) = 277.4 Hz, CF$_3$], 112.85 [q, J(F,C) = 27.3 Hz, C(Ph)CF$_3$], 18.86 [d, br, J(Rh,C) = 13.9 Hz, CH$_2$]; ^{19}F NMR (188.3 MHz, $CDCl_3$): $\delta = -59.44$ (s)

16: MS (70 eV): m/z 184 (M^+); IR (C_6H_6): $\tilde{\nu}$ [cm^{-1}] = 1955 (C=C=C); ^{1}H NMR (400 MHz, C_6D_6): $\delta = 4.75$ [q, J(F,H) = 3.2 Hz, CH$_2$]; ^{13}C NMR (100.6 MHz, C_6D_6): $\delta = 210.20$ [q, J(F,C) = 5.0 Hz, =C=], 124.19 [q, J(F,C) = 273.7 Hz, CF$_3$], 102.02 [q, J(F,C) = 32.2 Hz, C(Ph)CF$_3$], 83.12 (s, CH$_2$); ^{19}F NMR (188.3 MHz, C_6D_6): $\delta = -60.70$ (s)

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