Reactions of a Chelated Cyclopentadienylcobalt(I) Complex with 3,3-Disubstituted Cyclopropenes: Formation of Isoprene, Vinylcarbene, and 1-Phosphadiene Ligands at the Metal

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(Di-*tert*-butylphosphanyl-*P*-ethyl)cyclopentadienylcobalt(I) complexes **1** and **2** were treated with 3,3-disubstituted cyclopropenes to give isoprene and vinylcarbene complexes. The diphenylvinylcarbene complex reacted with *tert*-butylphosphaethyne to give unusual coupling products.

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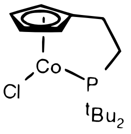
We have investigated the chemistry of (di-*tert*-butylphosphanyl-*P*-ethyl)cyclopentadienylcobalt(I) (Cp$^{\#}$Co) complexes for some time[1,2] and are particularly interested in reactions which are not observed with the unsubstituted cyclopentadienylcobalt(I) system (CpCo). As the Cp$^{\#}$Co system, in contrast to CpCo, does not facilitate cyclooligomerization reactions of alkynes, alkyne complexes are easily obtained with Cp$^{\#}$Co.[2] Recently, we reported the formation of Cp$^{\#}$Co vinylidene complexes.[3,4] Reactions with *tert*-butylphosphaethyne resulted in complete cleavage of the P≡C bond with formation of a phosphido cluster, whose phosphido ligand could be oxidized to a PO or PS ligand.[5] Cyclopropenes form complexes with transition metals or react with transition metal complexes to form oligomers[6−8] or vinylcarbene complexes.[9,10] Because only a few vinylcarbene complexes of cobalt are known[11,12] and in light of the role of vinylcarbene complexes in catalysis,[13] we undertook the preparation of such species by treatment of Cp$^{\#}$Co complexes such as **1** or **2** with cyclopropenes.



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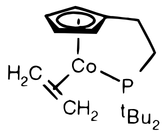

2

Treatment of cobalt chloride complex **1** with 3,3-dimethylcyclopropene[14,15] in the presence of sodium amalgam[4] gave 3,3-dimethylcyclopropene complex **3**,[16] which was characterized spectroscopically, in 71% yield. As a consequence of a DTA measurement (DTA = differential thermal analysis), **3** was heated at 65 °C in THF for 2 h to give isoprene complex **6** in 97% yield.[16] Although isoprene formation from 3,3-dimethylcyclopropene has been observed under pyrolytic conditions in up to 10% yield,[17,18] it is unprecedented in a metal-induced reaction under comparatively mild conditions.

We rationalize this reaction in terms of an insertion of the reduced cobalt species into one of the strained C−C single bonds of the cyclopropene with formation of a cobaltacyclobutene **4** as shown in Scheme 1. An intramolecular oxidative addition of one of the six equivalent C−H bonds (C−H activation) yields Co(III) complex **5** with a free phosphane arm. Subsequent reductive elimination gives isoprene complex **6**.

In contrast to the reaction with 3,3-dimethylcyclopropene, treatment of **2** with 3,3-diphenylcyclopropene,[15,19] which lacks C−H bonds at a carbon atom adjacent to the cyclopropene ring, resulted in the formation of diphenylvinylcarbene complex **7** in 91% yield, which was characterized spectroscopically.[20] We have been unable to isolate the 3,3-diphenylcyclopropene complex to date. However, in some experiments, a small amount of the

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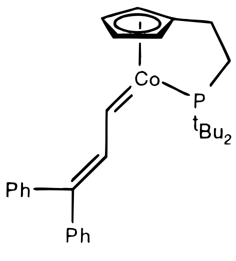
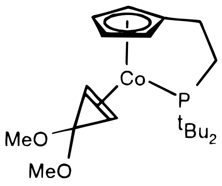
cobaltacyclobutene leading to **7** was isolated and identified by inspection of its spectroscopic data.



7

Reaction of cobalt chloride complex **1** with 3,3-dimethoxycyclopropene[21] gave a similar result; a mixture (5:1) of 3,3-dimethoxycyclopropene complex **8** and a not completely characterized side product was obtained in 93% yield. Presumably, the latter is the cobaltacyclobutene that might lead to the corresponding vinylcarbene complex. We are currently investigating this possibility and the chemistry of vinylcarbene complex **7**.



8

The first result in this context was obtained when **7** was treated with *tert*-butylphosphaethyne. Instead of a cobaltaphosphacyclobutene,[22] a mixture (3:1) was obtained in 65% overall yield, which consisted of coupling products **9** and **10**, Scheme 2. These were separated by column chromatography and subsequent crystallization.[23]

9 was characterized spectroscopically on the basis of the following considerations: The formula $C_{35}H_{47}CoP_2$ is confirmed by the mass spectrum showing the molecular ion peak at *m/z* 588 as well as by the high-resolution mass spectrum of this peak. The peak at *m/z* 296 confirms the existence of the Cp$^{\#}$Co fragment. In the ^{31}P NMR spectrum, the signal at $\delta = 29.2$ corresponds to an uncoordinated phosphane arm.[2,4] The ^{31}P NMR signal at δ −66.5 is assigned to the phosphorus atom in the coordinated C═P double bond, which is in the same range as the corresponding value of the conjugated system **10** (δ −11.5) and provides evidence against a cobaltaphosphacyclobutene substructure which should give rise to a signal at $\delta > 300$.[24,25] The ^{1}H NMR spectrum shows signals for all protons of **9** at reasonable

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(16) **3**: 3,3-Dimethylcyclopropene (245 mg, 3.60 mmol) was condensed into a −50 °C cold solution of **1** (301 mg, 0.90 mmol) in THF (50 mL). After 5 min, sodium amalgam (26.0 g, 2%) was added dropwise via pipet. The temperature was allowed to raise to −45 °C, causing the amalgam to melt. The mixture was stirred at this temperature for 10 min and was then allowed to warm to 20 °C. After the mixture was stirred for 1 h, the THF was condensed into a cold trap and the residue taken up with a small amount of diethyl ether and filtered through a P4 frit covered with a layer of Celite (3 cm). The Celite was washed with diethyl ether until the ether remained colorless. The diethyl ether was condensed into a cold trap, and the residue was crystallized from diethyl ether giving **3** (233 mg, 0.64 mmol, 71%) as brown crystals, mp 88 °C (DTA/TG), exothermic reaction. ^{1}H NMR (200 MHz, benzene-d_6): δ 1.14 (s, 3H, $\mathrm{C(C}\mathit{H}_3)_2$), 1.22 (d, 18H, $\mathrm{C(C}\mathit{H}_3)_3$, $^{3}J_{\mathrm{C,P}} = 11.5$ Hz), 1.38 (s, 3H, $\mathrm{C(C}\mathit{H}_3)_2$), 1.6−1.9 (m, 6H, $\mathrm{C}\mathit{H}_2\mathrm{C}\mathit{H}_2$, $\mathit{H}\mathrm{C{=}C}\mathit{H}$), 4.44 + 5.35 (AA′BB′ line system, 2 × 2H, Cp$^{\#}$-CH). ^{13}C NMR (50 MHz, benzene-d_6, APT): δ 24.61 (+, d, $\mathrm{PCH_2}\mathit{C}\mathrm{H_2}$, $^{2}J_{\mathrm{C,P}} = 6.5$ Hz), 24.62 (−, s, $\mathrm{C(}\mathit{C}\mathrm{H_3)_2}$), 26.8 (−, br d, ═$\mathit{C}$H, $^{2}J_{\mathrm{C,P}} = 8.0$ Hz), 30.5 (−, d, $\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$, $^{2}J_{\mathrm{C,P}} = 3.9$ Hz), 34.8 (−, d, $\mathrm{C(}\mathit{C}\mathrm{H_3)_2}$, $^{4}J_{\mathrm{C,P}} = 1.4$ Hz), 35.1 (+, d, $\mathit{C}\mathrm{(CH_3)_3}$, $^{1}J_{\mathrm{C,P}} = 6.3$ Hz), 37.3 (+, d, $\mathrm{P}\mathit{C}\mathrm{H_2CH_2}$, $^{1}J_{\mathrm{C,P}} = 20.7$ Hz), 48.28 (+, d, $\mathit{C}\mathrm{(CH_3)_2}$, $^{3}J_{\mathrm{C,P}} = 4.0$ Hz), 78.06 (−, d, Cp$^{\#}$-CH, $^{2}J_{\mathrm{C,P}} = 6.3$ Hz), 79.6 (−, s, Cp$^{\#}$-CH), 112.6 (+, d, Cp$^{\#}$-$\mathit{C}\mathrm{CH_2}$, $^{3}J_{\mathrm{C,P}} = 7.8$ Hz). ^{31}P NMR (81 MHz, benzene-d_6): δ 88.1. **6**: A solution of **3** (174 mg, 0.48 mmol) in toluene (5 mL) was heated at 65 °C for 2 h. The color changed from brown to red. The solvent was condensed into a cold trap, and the viscous residue was taken up with diethyl ether and filtered through a P4 frit covered with a layer of Celite (3 cm). The Celite was washed with diethyl ether until the ether remained colorless. The ether was condensed into a cold trap to give **6** (169 mg, 0.47, 97%) as a red oil. ^{1}H NMR (200 MHz, benzene-d_6): δ −0.26 (dd, 1H, $\mathrm{CH{=}C}\mathit{H}\mathrm{H}$, $^{3}J = 9$ Hz, $^{2}J = 1.5$ Hz), −0.16 (br s, 1H, $\mathrm{C(CH_3){=}C}\mathit{H}\mathrm{H}$), 1.20 (d, 18H, $\mathrm{C(C}\mathit{H}_3)_3$, $^{3}J_{\mathrm{P,H}} = 10.5$ Hz), 1.81 (m, 2H, $\mathrm{PCH_2C}\mathit{H}_2$), 1.82 (m, 1H, $\mathrm{CH{=}CH}\mathit{H}$), 1.85 (m, 1H, $\mathrm{C(CH_3){=}CH}\mathit{H}$), 2.11 (s, 3H, $\mathrm{C(C}\mathit{H}_3\mathrm{){=}CH_2}$), 2.65 (ddd, 2H, $\mathrm{PC}\mathit{H}_2\mathrm{CH_2}$, $^{2}J = 6.0$ Hz, $^{3}J = 7.0$ Hz, $^{2}J_{\mathrm{P,H}} = 18.0$ Hz), 4.48 (m, 1H, Cp$^{\#}$-CH), 4.57 (m, 1H, Cp$^{\#}$-CH), 4.70 (m, 1H, Cp$^{\#}$-CH), 4.77 (m, 1H, Cp$^{\#}$-CH), 4.93 (br m, 1H, $\mathrm{C}\mathit{H}\mathrm{{=}CH_2}$). ^{13}C NMR (100 MHz, benzene-d_6, BB): δ 23.1 (s, $\mathrm{C(}\mathit{C}\mathrm{H_3){=}CH_2}$), 23.6 (d, $\mathrm{PCH_2}\mathit{C}\mathrm{H_2}$, $^{2}J_{\mathrm{C,P}} = 23.3$ Hz), 29.8 (d, $\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$, $^{2}J_{\mathrm{C,P}} = 13.9$ Hz), 30.2 (d, $\mathrm{P}\mathit{C}\mathrm{H_2CH_2}$, $^{1}J_{\mathrm{C,P}} = 30.1$ Hz), 31.3 (d, $\mathit{C}\mathrm{(CH_3)_3}$, $^{1}J_{\mathrm{C,P}} = 22.9$ Hz), 31.5 (br s, ═$\mathit{C}\mathrm{H_2}$), 34.8 (br s, ═$\mathit{C}\mathrm{H_2}$), 78.6 (s, $\mathit{C}\mathrm{H{=}CH_2}$), 78.9 (s, Cp$^{\#}$-$\mathit{C}$H), 79.0 (s, Cp$^{\#}$-$\mathit{C}$H), 79.9 (s, Cp$^{\#}$-$\mathit{C}$H), 80.2 (s, Cp$^{\#}$-$\mathit{C}$H), 93.7 ($\mathrm{C(CH_3){=}CH_2}$), 101.3 (d, Cp$^{\#}$-$\mathit{C}\mathrm{CH_2}$, $^{3}J_{\mathrm{C,P}} = 15.7$ Hz). ^{31}P NMR (81 MHz, benzene-d_6): δ 29.3.

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(20) **7**: A solution of 3,3-diphenylcyclopropene (2.12 g, 11.0 mmol) and **2** (3.60 g, 11.0 mmol) in THF (750 mL) was stirred at 20 °C for 12 h. The color changed from red-brown to deep green. The solvent was condensed into a cold trap, and the residue was taken up with a small amount of THF, filtered through a P4 frit covered with a layer of Celite (3 cm). The Celite was washed with THF until the filtrate remained colorless. The solvent was condensed into a cold trap, and **7** (4.88 g, 10.0 mmol, 91%) was obtained as green-black crystals, mp 154.2 °C (DTA/TG), exothermic reaction. ^{1}H NMR (200 MHz, benzene-d_6): δ 1.07 (d, 18H, $\mathrm{C(C}\mathit{H}_3)_3$, $^{3}J_{\mathrm{P,H}} = 12.0$ Hz), 1.82−2.15 (m, 2H, $\mathrm{PCH_2C}\mathit{H}_2$), 2.65 (dt, 2H, $\mathrm{PC}\mathit{H}_2\mathrm{CH_2}$, $^{3}J = 8$ Hz, $^{2}J_{\mathrm{P,H}} = 8$ Hz), 3.85 (m, 2H, Cp$^{\#}$-CH), 5.80 (m, 2H, Cp$^{\#}$-CH), 6.95−7.52 (m, 8H, arom. CH), 8.14 (br d, 2H, arom. CH), 8.32 (br d, 1H, $\mathrm{Co{=}CH{-}C}\mathit{H}{=}$, $^{3}J = 14.0$ Hz), 11.62 (dd, 1H, $\mathrm{Co{=}C}\mathit{H}\mathrm{{-}CH}{=}$, $^{3}J = 14.0$ Hz, $^{2}J_{\mathrm{P,H}} = 29.0$ Hz). ^{13}C NMR (100 MHz, benzene-d_6): δ 25.1 (d, $\mathrm{PCH_2}\mathit{C}\mathrm{H_2}$, $^{2}J_{\mathrm{P,C}} = 6.0$ Hz), 29.5 (d, $\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$, $^{2}J_{\mathrm{P,C}} = 4.4$ Hz), 34.7 (d, $\mathit{C}\mathrm{(CH_3)_3}$, $^{1}J_{\mathrm{P,C}} = 10.9$ Hz), 40.15 (d, $\mathrm{P}\mathit{C}\mathrm{H_2CH_2}$, $^{1}J_{\mathrm{P,C}} = 19.6$ Hz), 78.5 (Cp$^{\#}$-CH), 81.2 (d, Cp$^{\#}$-CH, $^{2}J_{\mathrm{C,P}} = 6$ Hz), 107.6 (d, Cp$^{\#}$-$\mathit{C}\mathrm{CH_2}$, $^{3}J_{\mathrm{P,C}} = 7.1$ Hz), 123.6 (d, $\mathit{C}\mathrm{Ph_2}$, $^{4}J_{\mathrm{C,P}} = 8.2$ Hz), 125.4 (arom. CH), 125.7 (arom. CH), 125.8 (arom. CH), 146.6 (d, arom. *ipso-C*, $^{5}J_{\mathrm{C,P}} = 2, 2$ Hz), 148.6 (d, arom. *ipso-C*, $^{5}J_{\mathrm{C,P}} = 2.2$ Hz), 155.9 (d, $\mathrm{Co{=}CH{=}}\mathit{C}\mathrm{H}$, $^{3}J_{\mathrm{C,P}} = 2.7$ Hz), 199.5 (d, $\mathrm{Co{=}}\mathit{C}\mathrm{H{=}CH}$, $^{2}J_{\mathrm{C,P}} = 33.8$ Hz). ^{31}P NMR (81 MHz, benzene-d_6): δ 89.9.

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(23) Reaction of **7** wih *tert*-butylphosphaethyne: *tert*-Butylphosphaethyne (2.6 mg, 0.26 mmol) was added to a solution of **7** (120 mg, 0.26 mmol) in THF (5 mL). After 3 days of stirring, a color change from green to brown was completed. The THF was condensed into a cold trap, and the residue was taken up with petroleum ether/diethyl ether (3:1) and chromatographed (SiO_2). The isolated material was crystallized from diethyl ether to give the first fraction of **9** (74 mg, 0.13 mmol, 49%) as red crystals, mp 159 °C (DSC). ^{1}H NMR (400 MHz, benzene-d_6): δ 1.18 (d, 9H, $\mathrm{C(C}\mathit{H})_3$, $^{3}J_{\mathrm{C,P}} = 10.6$ Hz), 1.19 (d, $\mathrm{C(C}\mathit{H})_3$, $^{3}J_{\mathrm{C,P}} = 10.7$ Hz), 1.37 (s, 9H, $\mathrm{C(C}\mathit{H}_3)_3$), 1.61 (m, 2H, $\mathrm{C}\mathit{H}_2$), 2.50 (m, 2H, $\mathrm{C}\mathit{H}_2$), 3.43 (m, 1H, phosphirene-CH, $J = 3.3$ Hz), 4.23 (m, 1H, Cp$^{\#}$-CH), 4.63 (m, 1H, Cp$^{\#}$-CH), 4.78 (m, 2H, Cp$^{\#}$-CH), 5.37 (m, 1H, ═CH, $J = 3.3$ Hz), 6.94 (m, 1H, arom. H), 7.10−7.25 (4H, arom. H), 7.30−7.44 (m, 3H, arom. H), 7.72 (m, 2H, arom. H). ^{13}C NMR (100 MHz, benzene-d_6): δ 23.2 (d, $\mathrm{PCH_2}\mathit{C}\mathrm{H_2}$, $^{2}J_{\mathrm{C,P}} = 23.5$ Hz), 23.3 (d, $\mathrm{P}\mathit{C}\mathrm{H_2CH_2}$, $^{2}J_{\mathrm{C,P}} = 23.5$ Hz), 29.8 (d, $\mathrm{PC(}\mathit{C}\mathrm{H_3)_3}$, $^{2}J_{\mathrm{C,P}} = 14.0$ Hz), 29.9 (d, $\mathrm{PC(}\mathit{C}\mathrm{H_3)_3}$, $^{2}J_{\mathrm{C,P}} = 14.0$ Hz), 30.7 (d, $\mathrm{C}\mathit{C}\mathrm{(C_3)_3}$, $J_{\mathrm{C,P}} = 1.5$ Hz), 31.3 (d, $\mathrm{P}\mathit{C}\mathrm{(CH_3)_3}$, $^{1}J_{\mathrm{C,P}} = 22.3$ Hz), 32.1 (d, $\mathrm{CC(}\mathit{C}\mathrm{H_3)_3}$, $^{3}J_{\mathrm{C,P}} = 5.1$ Hz), 34.0 (d, $\mathrm{P}\mathit{C}\mathrm{(CH_3)_3}$, $^{1}J_{\mathrm{C,P}} = 9.5$ Hz), 39.1 (═CH), 51.3 (d, PCH, $^{1}J_{\mathrm{C,P}} = 3.2$ Hz), 66.3 (d, P═C, $J_{\mathrm{C,P}} = 27.0$ Hz), 78.2 (d, Cp$^{\#}$-CH, $^{2}J_{\mathrm{C,P}} = 2.4$ Hz), 79.6 (d, Cp$^{\#}$-CH), 79.8 (d, Cp$^{\#}$-CH, $^{2}J_{\mathrm{C,P}} = 1.9$ Hz), 81.3 (d, Cp$^{\#}$-CH, $^{2}J_{\mathrm{C,P}} = 6.4$), 103.4 (d, Cp$^{\#}$-$\mathit{C}$-CH$_2$, $^{3}J_{\mathrm{C,P}} = 15.0$ Hz), 113.3 ($\mathrm{Ph_2}\mathit{C}\mathrm{{=}C}$), 124.9 (arom. CH), 125.92 (arom. CH), 125.95 (arom. CH), 126.1 (arom. CH), 127.9 (arom. CH), 128.0 (arom. CH), 128.7 (arom. CH), 128.8 (arom. CH), 129.4 (arom. CH), 129.5 (arom. CH), 131.6 (arom. CH), 147.5 (*ipso-C*, $^{3}J_{\mathrm{C,P}} = 12.7$ Hz), 151.7 (*ipso-C*, $^{3}J_{\mathrm{C,P}} = 1.9$ Hz). ^{31}P NMR (162 MHz, benzene-d_6): δ 29.2 ($\mathit{P}\mathrm{(CCH_3)_3}$), −66.5 (phosphirene-*P*). Second crystal fraction: **10** (29 mg, 0.04 mmol, 16%).

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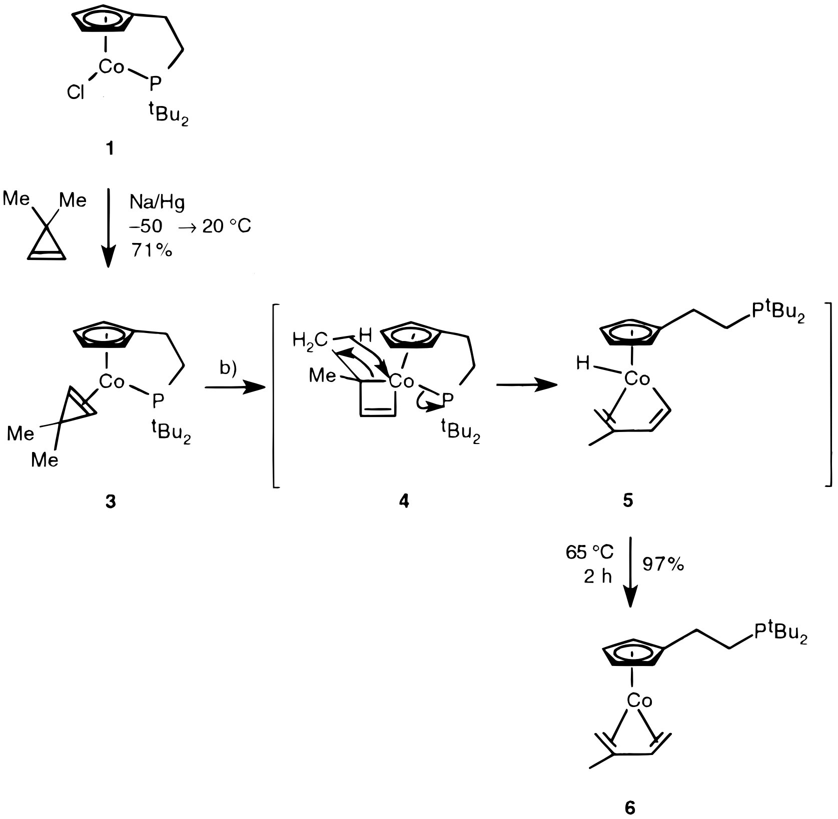
Scheme 1



chemical shifts. In addition to the usual signals of the Cp$^{\#}$Co fragment, the signals of the coordinated =C*H* at δ 5.37 (J = 3.3 Hz) and one of the adjacent tertiary phosphirene C*H* at δ 4.43 (J = 3.3 Hz) are diagnostic. In the ^{13}C NMR spectrum, the signals for all carbon atoms are found and assigned on the basis of DEPT spectra. The assignment of the coordinated olefinic =*C*H (δ 39.1) and the phosphirene *C*H (δ 51.3) is based on the observation of a C,P coupling (J = 3.2 Hz) at the latter signal.

The structure of **10** was determined by a crystal structure analysis (Figure 1).[26] Complex **10** is a 1,2-*cis*-disubstituted 1-phosphadiene. The P=C bond distance (1.781(4) Å) is between the average values of P−C single (1.85 Å) and P=C double bonds (1.67 Å).[27] There is one preliminary communication describing a bimetallic η^2 (P=C) platinum complex of a 1-phosphadiene with the phosphorus atom coordinated to tungsten.[28] The additional coordination of the ligand to tungsten makes this structure and that of **10** only partly comparable. The P=C double bond in the platinum complex is 1.833(8) Å, as compared to 1.781(4) Å in **10**. This is in accord

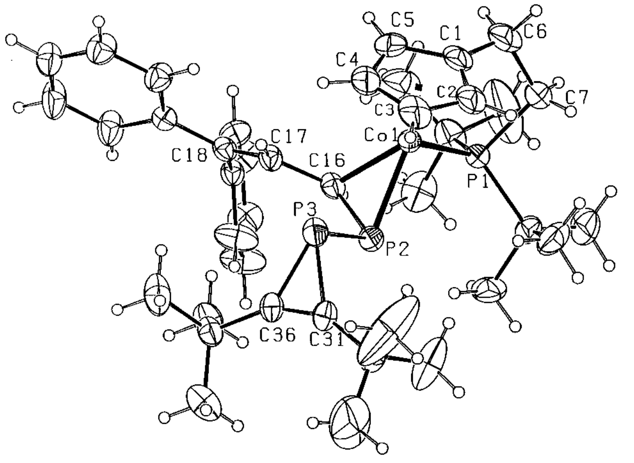


Figure 1. Crystal structure of **10**. Selected bond lengths (Å) and angles (deg): Co1−P1 2.221(1), Co1−P2 2.257(1), P2−P3 2.237(1), P2−C16 1.781(4), P3−C31 1.848(4), P3−C36 1.836(4), C16−C17 1.454(5), C17−C18 1.351(5), C31−C36 1.282(5); P1−Co1−P2 102.4(1), P2−Co1−C16 48.5(1), Co1−P2−P3 105.4(1), Co1−P2−C16 59.9(1), P3−P2−C16 105.4(1), P2−C16−C17 125.3(3), Co1−C16−C17 118.3(3), C16−C17−C18 127.9(3), C31−P3−C36 40.74(16), P3−C31−C36 69.1(2), P3−C36−C31 70.1(2).

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[26] Crystal structure analysis of **10**: Crystal size 0.13 × 0.74 × 0.28 mm, crystal system monoclinic, space group $P2_1/c$ (No. 14), a = 18.589(3) Å, b = 11.606(2), c = 18.457(3) Å, β = 103.57(2)°, V = 3870.8(12) Å^3, Z = 4, ρ_{calc} = 1.182 g/cm^3, $2\theta_{\max}$ = 48.2°, Mo Kα radiation, λ = 0.710 73 Å, 159 imaging plates, $\Delta\phi$ = 1.0°, T = 300 K, 19 351 measured reflections, 5711 independent reflections, 5711 reflections used for refinement, σ-limit 0 for refinement, no absorption correction, structure solution with direct methods with SHELXS-86, refinement with SHELXL-93, 401 free parameters, hydrogen atoms in geometrically calculated positions, H27 (bound at C16) independently refined, R1 = 0.0413 [$I > 2\sigma(I)$], wR2 = 0.0944 (all data), refinement on F^2, minimal and maximal residual eletron density −0.26, 0.26 e/Å^3. The crystallographic data (without structure factors) of the structure described in this publication were deposited as supplementary publication no. CCDC 100140 at the Cambridge Crystallography Data Centre. Copies of the data can be obtained with no charge from the following address in Great Britain: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ (Telefax Int. +1223/336−033. E-mail: deposit@ccdc.cam.ac.uk).

[27] *Multiple Bonds and Low Coordination in Phosphorous Chemistry*; Regitz, M., Scherer, O. J., Ed.; Georg Thieme Verlag: Stuttgart, 1990.

[28] Ajulu, F. A.; Al-Juaid, S. S.; Carmichael, D.; Hitchcock, P. B.; Meidine, M. F.; Nixon, J. F.; Mathey, F.; Huy, N. H. T. *J. Organomet. Chem.* **1991**, *406*, C20. We thank one of the reviewers for drawing our attention to this publication.

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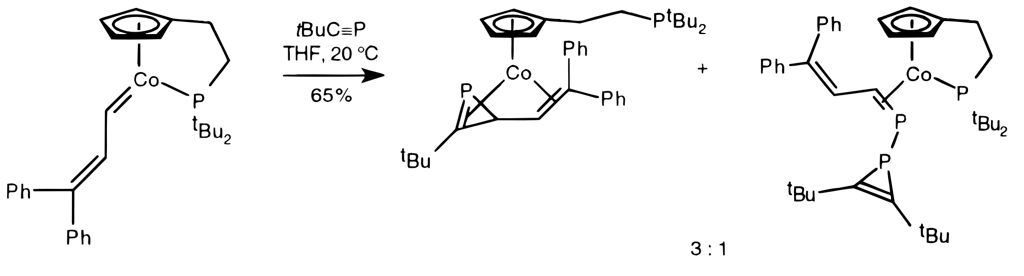
Scheme 2



7 **9** **10**

with the fact that the ethene C═C double bond in $(Ph_3P)_2Pt(C_2H_4)$ is somewhat longer (1.434(13) Å)[29] than that in **2** (1.396(5) Å);[3] however, the large estimated standard deviation of the analysis of $(Ph_3P)_2Pt(C_2H_4)$ limits the meaning of such a comparison.

The formation of main product **9** can be explained by assuming a cycloaddition of the vinylcarbene in **7** and the P≡C triple bond.[27] To explain the formation of 1-phosphadiene **10**, which is a 1:2 adduct of **7** and *tert*-butylphosphaethyne, we envisage a dimerization of the phosphaethyne to complex **11**.[27,30] From **11**, the formation of **12** with recomplexation of the phosphane arm can be explained as shown. A stepwise mechanism via a phosphinidene complex **12** would be in accord with observations of Mathey et al. with chromium and tungsten complexes.[31]

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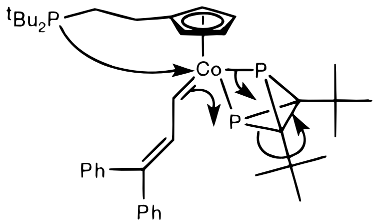
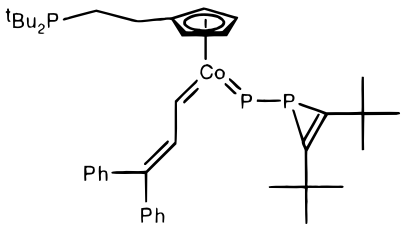


11



12

Supporting Information Available: Text giving the analytical data of the new compounds, tables of crystal data, final coordinates, hydrogen atom positions, anisotropic thermal parameters, bond distances, bond angles, and torsion angles, and NMR spectra (52 pages). Ordering information is given on any current masthead page.

OM970851O

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[30] Nixon, J. F. *Chem. Soc. Rev.* **1995**, 319.

[31] Huy, N. H. T.; Ricard, L.; Mathey, F. *Organometallics* **1988**, *7*, 1791.