

Notes

2,3-Benzo-7-phosphanorbornadiene Complexes: Synthesis and Chemistry

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Summary: The reaction of benzyne with 3,4-dimethylphosphole pentacarbonylmolybdenum complexes affords the corresponding 2,3-benzo-7-phosphanorbornadiene complexes through [4+2] cycloaddition. The condensation takes place on the less hindered side of the phosphole ring corresponding to the phosphorus substituent as shown by the X-ray crystal structure analysis of the phenyl derivative (**2**). The strain at the bridge of **2** (C–P–C angle ca. 80°) induces a variety of splitting reactions. Upon decomplexation by dppe at 110 °C in toluene, phenylphosphinidene is generated and recovered as phenylphosphine. Upon sulfuration under the same conditions, [PhPS₂] is formed and trapped as a [4+2] adduct with 2,3-dimethylbutadiene. Potassium *tert*-butylate attacks the bridge in THF at –78 °C and, after methylation and hydrolytic workup, yields [Ph(Me)P(OH)Mo(CO)₅].

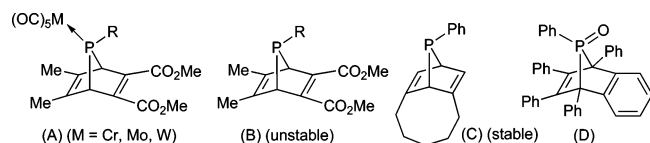
In fact, all the attempts to liberate 7-phosphanorbornadienes from their complexes have failed: these species are highly unstable, and it is necessary to reduce the aromatic stabilization of the arene byproduct of their decomposition as in **C** to allow their isolation. This has been achieved by distorting the arene planar structure and, thus, reducing its aromatic stabilization energy.⁴ Another, less sophisticated approach could rely on the benzo-annellation of the arene byproduct. The description in the literature of a quite stable 2,3-benzo-7-phosphanorbornadiene 7-oxide (**D**)⁵ seems to validate this idea. In this report, we describe the synthesis of a series of 2,3-benzo-7-phosphanorbornadiene complexes and various reactions leading to the splitting of their phosphorus bridge.

Introduction

Even though they have been the subject of numerous theoretical studies, the chemistry of phosphinidenes [R–P] remains poorly developed due to the lack of general methods for synthesizing them under mild conditions.¹ The most promising results in this respect are those of Gaspar and his group, who were able to generate mesitylphosphinidene by photolysis of 1-mesitylphosphirane at low temperature.² Unfortunately, this approach cannot be generalized for the generation of alkylphosphinidenes. The situation is much more favorable for electrophilic terminal phosphinidene complexes [RP–M(CO)₅] (M = Cr, Mo, W) that display a rich carbene-like chemistry and can be generated with a huge variety of substituents from the appropriate 7-phosphanorbornadiene complexes **A**.³ Inevitably, this comparison leads one to wonder why it would not be possible to use noncomplexed 7-phosphanorbornadienes **B** as precursors for phosphinidenes.

Results and Discussion

Since our aim was to preserve the variety of substituents that characterize the 7-phosphanorbornadiene route to terminal phosphinidene complexes, we chose to investigate the reaction of the highly reactive benzyne with phosphole derivatives, the use of phospholes granting this variety. We selected the 1-R-3,4-dimethylphosphole molybdenumpentacarbonyl complexes as the dienes, the dimethyl substitution enhancing the reactivity of the poorly reactive ring dienic subunit and the choice of molybdenum for the protection of the phosphorus lone pair facilitating the subsequent decomplexation step. The generation of benzyne was performed through the reaction of anthranilic acid and isoamyl nitrite in toluene at 40 °C.⁶ The reaction with 1-phenyl-3,4-dimethylphosphole pentacarbonylmolybdenum (**1**) is clean according to the monitoring of the mixture by ³¹P NMR, but slow and stops at ca. 50% conversion, sug-



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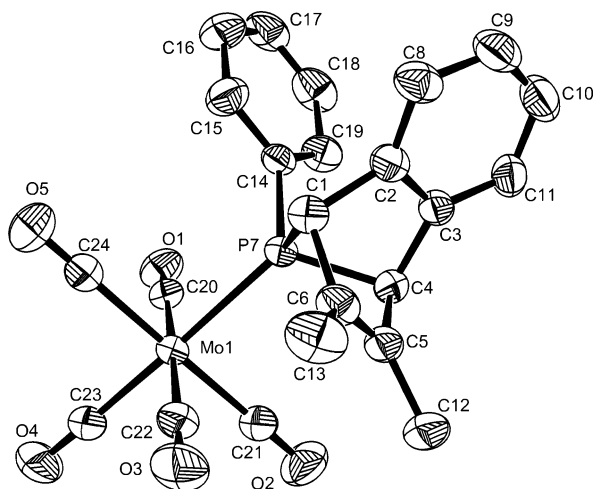
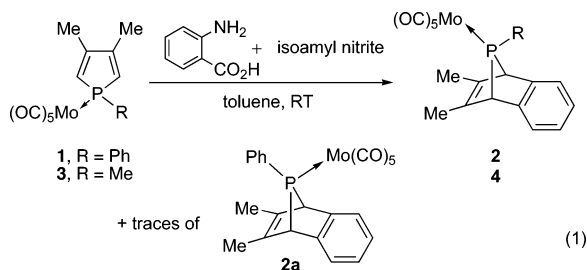


Figure 1. ORTEP drawing of one molecule of **2**. Main bond lengths (Å) and angles (deg): P(7)–Mo(1) 2.4971(12), P(7)–C(1) 1.887(2), P(7)–C(4) 1.8708(19), P(7)–C(14) 1.8199(19), C(1)–C(2) 1.511(3), C(2)–C(3) 1.403(3), C(3)–C(4) 1.510(3), C(4)–C(5) 1.534(3), C(5)–C(6) 1.334(3), C(6)–C(1) 1.528(3); C(1)–P(7)–C(4) 80.07(8), Mo(1)–P(7)–C(1) 124.70(6), Mo(1)–P(7)–C(4) 119.78(6), Mo(1)–P(7)–C(14) 114.37(6), C(1)–P(7)–C(14) 104.45(8), C(4)–P(7)–C(14) 108.15(9).

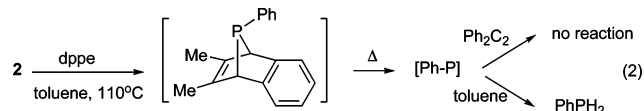
gesting the formation of an inhibitor as a minor byproduct. Modifying the dilution, the excess and the ratio of the benzyne precursors, or the temperature, or using various catalysts never allowed us to improve the yield of the [4+2] adduct **2** (eq 1), which stayed below 25% when excluding the possible recovery of the unreacted starting product. Molybdenum hexacarbonyl is known to interact with N–O bonds and carboxylic acids, and this might explain this limitation. The use of tungsten–carbonyl derivatives did not improve the situation.



The cycloadduct **2** is characterized by the low-field shift of its ^{31}P resonance: $\delta^{31}\text{P}(\mathbf{2})$ 196 (CDCl_3). It is accompanied by ca. 12% of an inseparable isomer **2a**, which likely corresponds to the condensation of benzyne on the other face of phosphole **1**: $\delta^{31}\text{P}(\mathbf{2a})$ 216 (CDCl_3). The mass spectrum (FAB) shows the molecular peak of **2** at m/z 502 (^{98}Mo) and the $M - 5\text{CO}$ peak at m/z 362, together with the peaks corresponding to the terminal phosphinidene complex $[\text{PhP} - \text{Mo}(\text{CO})_5]$ at m/z 346 (molecular peak) and 318 ($M - \text{CO}$, base peak). These spectral characteristics are very similar to those of nonannellated 7-phosphanorbornadiene complexes.⁷ The stereochemistry of **2** was established by an X-ray crystal structure analysis (Figure 1). As expected on steric grounds, the benzyne reacts on the least hindered side of the phosphole ring corresponding to the phenyl

substituent. At 80°, the C(1)–P(7)–C(4) bridge angle is similar to that found in a 7-phosphanorbornadiene complex.⁷ The stereochemistry of **2** has an interesting spectral consequence: the sp^2 carbons carrying the methyl substituents resonate at 139.06 ppm (established by ^1H – ^{13}C correlation) and display a sizable coupling with phosphorus (16.1 Hz). The carbons at the junction with the benzo ring resonate at 145.73 and show no coupling with phosphorus. According to our expectations, the generalization of the condensation reaction with other phosphorus substituents (methyl) was straightforward.

The next step of our study concerned the various potential methods for decomplexing and splitting the bridge phosphorus unit and trapping it with various reagents. The study was carried out with **2**. It must immediately be stressed that the thermal stability of the 2,3-benzo-7-phosphanorbornadiene complexes is substantially higher than that of the corresponding 7-phosphanorbornadiene complexes. At 110 °C in boiling toluene, no decomposition is observed, whereas 7-phosphanorbornadiene complexes collapse under these conditions. At 140 °C in boiling xylene, decomposition slowly takes place, but trapping the phosphinidene unit by tolan proved to be impossible. The decomplexation of $[\text{P} - \text{Mo}(\text{CO})_5]$ complexes by reaction with 1,2-bis-(diphenylphosphino)ethane (dppe) is a well-established technique.³ Accordingly, we allowed **2** to react with dppe in boiling toluene in the presence of tolan as a trapping reagent (eq 2).



Monitoring the reaction mixture by ^{31}P NMR showed that the decomplexation indeed takes place, as demonstrated by the formation of $[\text{Mo}(\text{dppe})(\text{CO})_4]$ ($\delta^{31}\text{P}$ 57.3). The free 2,3-benzo-7-phosphanorbornadiene thus formed immediately collapses, but the resulting phenylphosphinidene does not react with tolan to give the expected phosphirene but, instead, abstracts hydrogen from toluene to give phenylphosphine, which is identified by its characteristic triplet: $\delta^{31}\text{P}(\text{PhPH}_2)$ –123 ($^1J_{\text{H-P}} = 200$ Hz). This result is coherent with the triplet ground state of phenylphosphinidene,⁸ but comes in sharp contrast with the reactivity of mesitylphosphinidene as formed by UV splitting of 1-mesitylphosphirane at low temperature.² We suggest that the experiments of Gaspar initially produce the mesitylphosphinidene as a singlet excited state, which reacts, for example, with 2,3-dimethylbutadiene to give the corresponding 2-vinylphosphirane (and not the phospholene as expected for a triplet). In the absence of trapping reagent, deexcitation takes place to give the ground state triplet that has been characterized by ESR. It is interesting to note in this context that the singlet excited state of a dialkylsilylene has been found responsible for its photoreactions.⁹

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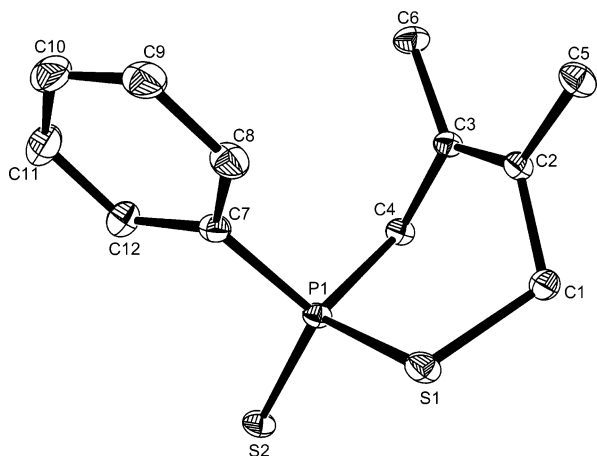
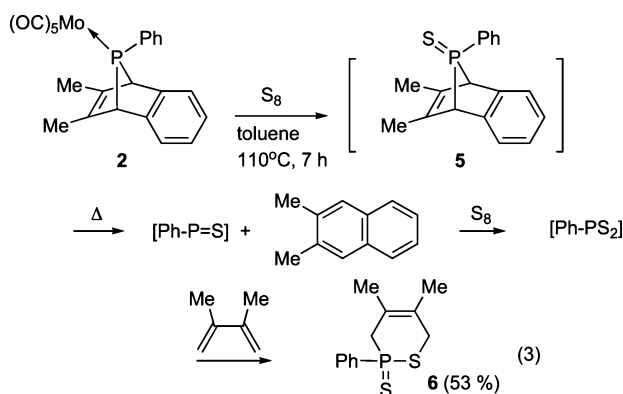


Figure 2. ORTEP drawing of one molecule of **6**. Main bond lengths (Å) and angles (deg): P(1)–S(1) 2.0922(3), P(1)–S(2) 1.9524(3), P(1)–C(4) 1.8309(6), P(1)–C(7) 1.8170(7), S(1)–C(1) 1.8494(7), C(1)–C(2) 1.5053(9), C(2)–C(3) 1.3447(9), C(3)–C(4) 1.5080(8); C(7)–P(1)–C(4) 105.37(3), C(7)–P(1)–S(2) 112.24(2), C(4)–P(1)–S(2) 113.63(2), C(7)–P(1)–S(1) 107.54(2), C(4)–P(1)–S(1) 101.71(2), S(2)–P(1)–S(1) 115.369(11), C(1)–S(1)–P(1) 99.51(2), C(2)–C(1)–S(1) 113.28(5), C(3)–C(4)–P(1) 111.79(4).

Another well-documented method for removing molybdenum from its $[P-Mo(CO)_5]$ complexes is sulfurization.³ In our case, the reaction proceeds cleanly in boiling toluene to give $[PhPS_2]$, which is trapped by 2,3-dimethylbutadiene (eq 3).



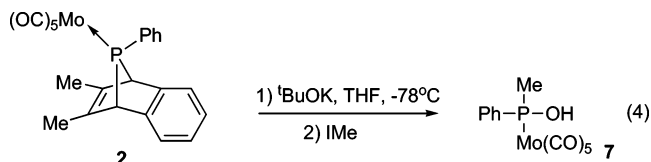
To our surprise, we were unable to detect by ^{31}P NMR spectroscopy the formation of the intermediate sulfide **5**, whose decomposition is instantaneous at 110 °C. Since phenylphosphinidene sulfide is known to react with 2,3-dimethylbutadiene to give the corresponding phospholene sulfide,¹⁰ its reaction with sulfur appears to be faster than its reaction with the diene. Once the phenyldithioxophosphorane is formed, it is trapped by 2,3-dimethylbutadiene to give the corresponding [4+2] adduct. A stable, bulky aryldithioxophosphorane has been shown to react similarly with 2,3-dimethylbutadiene.¹¹ The final product (**6**) has been described in the literature and partly characterized.¹² We provide here some additional data, including an X-ray crystal structure analysis (Figure 2). The dimethylnaphthalene byproduct has also been characterized. The structure

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of the hetero-ring of **6** is folded, the C(1)–S(1)–P(1)–C(4) plane making an angle of 122.9° with the C(1)–C(2)–C(3)–C(4) plane. Apparently, the diene has approached the reacting P=S bond from the side of the phenyl substituent, contrary to what we expected on steric grounds.

Weak nucleophiles are known to split the phosphorus bridge of 7-phosphanorbornadiene complexes under mild conditions,¹³ probably through a retro-McCormack mechanism. A weak nucleophile such as the malonate anion does not react with **2**, but a stronger one such as t BuOK does split the bridge as expected (eq 4).



In view of the reaction conditions, a phosphinidene mechanism is excluded. The initial attack at phosphorus by the nucleophile likely produces an anionic pentacoordinate phosphorus species that undergoes a reductive elimination of dimethylnaphthalene.¹⁴ The hydrolysis of the P–O t Bu bond probably takes place during the workup. It must be stressed here that strong nucleophiles do not split the phosphorus bridge but attack the electron-poor double bond of 2,3-bis(methoxycarbonyl)-7-phosphanorbornadiene complexes.

Finally, even though they cannot be used as useful phosphinidene precursors, 2,3-benzo-7-phosphanorbornadiene complexes such as **2** display an interesting variety of splitting reactions.

Experimental Section

Reactions were performed under nitrogen using oven-dried glassware. Dry tetrahydrofuran was obtained by distillation from Na/benzophenone. Silica gel (70–230 mesh) was used for chromatographic separation. Nuclear magnetic resonance spectra were obtained on a Bruker Avance 3000 and Varian Inova spectrometer operating at 300.13 MHz for 1H , 75.45 MHz for ^{13}C , and 121.496 MHz for ^{31}P . Chemical shifts are expressed in parts per million downfield from external TMS (1H and ^{13}C) and external 85% H_3PO_4 (^{31}P). Mass spectra were obtained on VG 7070 and Hewlett-Packard 5989A GC/MS spectrometers. Elemental analyses were performed by Desert Analytics Laboratory, Tucson, AZ. Starting materials were obtained from commercial suppliers.

Synthesis of 2,3-Benzo-7-phosphanorbornadiene Complex 2. A solution of complex **1** (2 g, 4.71×10^{-3} mol) in toluene (160 mL) was mixed with anthranilic acid (646 mg, 4.71×10^{-3} mol) in acetone (4 mL). Immediately after, isoamyl nitrite was added (2 mL, 14.15×10^{-3} mol) at one time. The solution was stirred for 30 min at room temperature, then was heated at 40 °C during one night. After evaporation, the residue was chromatographed on silica gel with hexane as the eluent. The benzo-7-phosphanorbornadiene **2** was thus obtained as brown crystals in 19.5% yield (0.46 g). The starting phosphole complex **1** was also recovered (1.31 g), giving a conversion yield of 56%.

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^{31}P NMR (CDCl_3): δ 196.0 and 216.3. ^1H NMR (CDCl_3): δ 2.01 (s, 6H, CH_3), 3.87 (d, 2H, $^2J_{\text{P-H}} = 3.5$ Hz, CH bridge), 7.11 (m, 9H, H benzo and phenyl rings). ^{13}C NMR (CDCl_3): δ 15.67 (s, CH_3), 57.49 (d, $^1J_{\text{P-C}} = 18.4$ Hz, CH bridge), 123.08 (s, C_8 , C_{11}), 125.28 (s, C_9 , C_{10}), 128.45 (m, phenyl), 139.06 (d, $^2J_{\text{P-C}} = 16.1$ Hz, C_5 , C_6), 145.73 (s, C_2 , C_3), 205.49 (d, $^2J_{\text{P-C}} = 9.2$ Hz, CO cis), 209.93 (d, $^2J_{\text{P-C}} = 25.3$ Hz, CO trans). EIMS: m/z 502 (M^+ , 7%), 472 ($\text{M} - \text{CO}$, 7%), 418 ($\text{M} - 3\text{CO}$, 20%), 360 ($\text{M} - 5\text{CO}$, 38%), 346 ($[\text{Ph} - \text{P} - \text{Mo}(\text{CO})_5]^+$, 57%), 318 ($[\text{Ph} - \text{P} - \text{Mo}(\text{CO})_4]^+$, 61%). Anal. Calcd for $\text{C}_{23}\text{H}_{17}\text{O}_5\text{PMo}$: C, 55.22; H, 3.42. Found: C, 55.28; H, 3.48.

Synthesis of 2,3-Benzo-7-phosphanorbornadiene Complex 4. The same procedure as above for complex 3 was used (yield 8.5%). ^{31}P NMR (CDCl_3): δ 180.2. ^1H NMR (CDCl_3): δ 1.12 (d, 3H, $^2J_{\text{P-H}} = 4.1$ Hz, P- CH_3), 1.94 (2s, 6H, $\text{H}_3\text{C}-\text{C}=\text{C}-\text{CH}_3$), 3.46 (d, 2H, $^2J_{\text{P-H}} = 4.1$ Hz, CH bridge), 7.08 (m, C_8 -H, C_9 -H), 7.29 (m, C_7 -H, C_{10} -H). ^{13}C NMR (CDCl_3): δ 15.44 (s, $\text{H}_3\text{C}-\text{C}=\text{C}-\text{CH}_3$), 20.12 (s, P- CH_3), 57.91 (d, $^2J_{\text{P-C}} = 19.6$ Hz, CH bridge), 123.52 (s, C_9 -H, C_{10} -H), 125.62 (s, C_8 -H, C_{11} -H), 139.61 (d, $^2J_{\text{P-C}} = 16.1$ Hz, C_5 and C_6), 145.71 (s, C_2 and C_3), 205.80 (d, $^2J_{\text{P-C}} = 8.1$ Hz, CO cis), 209.59 (d, $^2J_{\text{P-C}} = 25.3$ Hz, CO trans). EIMS: m/z 440 (M^+ , 35%), 412 ($\text{M} - \text{CO}$, 34%), 356 ($\text{M} - 3\text{CO}$, 62%), 326 ($\text{M} - 4\text{CO}$, 37%), 298 ($\text{M} - 5\text{CO}$, 58%), 284 ($[\text{CH}_3 - \text{P} - \text{Mo}(\text{CO})_5]^+$, 100%), 256 ($[\text{CH}_3 - \text{P} - \text{Mo}(\text{CO})_4]^+$, 68%). Anal. Calcd for $\text{C}_{18}\text{H}_{15}\text{O}_5\text{PMo}$: C, 49.33; H, 3.45. Found: C, 49.05; H, 3.20.

Synthesis of 2-Phenyl-4,5-dimethyl-1-thia-2-phospha-cyclohex-4-ene-2-sulfide, 6. A solution of complex 2 (100 mg, 0.2×10^{-3} mol), sulfur (51.2 mg, 1.6×10^{-3} mol), and 2,3-dimethylbutadiene (181 μL , 1.6×10^{-3} mol) in toluene (2 mL) was heated at 110 $^\circ\text{C}$ for 7 h. After evaporation, the residue was chromatographed on silica gel with hexane/dichloromethane (3/7) as the eluent. The product was thus obtained as dark brown crystals in 53% yield (27 mg). Dimethylnaphthalene was also recovered as white crystals in 64% yield (20 mg) and identified by ^1H NMR, ^{13}C NMR, and mass spectrometry. ^{31}P NMR (CDCl_3): δ 66.4. ^1H NMR (CDCl_3): δ 1.64 (s, S- $\text{CH}_2\text{-C-CH}_3$), 1.92 (d, 3H, $^4J_{\text{P-H}} = 5.3$ Hz, P- $\text{CH}_2\text{-C-CH}_3$), 2.97 (m, 2H, P- CH_2), 3.33 (dd, 1H, $^3J_{\text{P-H}} = 20.2$ Hz, $^2J_{\text{H-H}} = 15.1$ Hz, P-S- CH_2), 3.67 (dd, 1H, $^3J_{\text{P-H}} = 15.1$ Hz, $^2J_{\text{H-H}} = 15.1$ Hz, P-S- CH_2), 7.71 (m, 5H, P- C_6H_5). ^{13}C NMR (CDCl_3): δ 19.73 (s, S- $\text{CH}_2\text{-C-CH}_3$), 21.42 (d, $^3J_{\text{P-C}} = 5.7$ Hz, P- $\text{CH}_2\text{-C-CH}_3$), 35.21 (d, $^2J_{\text{P-C}} = 5.7$ Hz, S- CH_2), 45.37 (d, $^1J_{\text{P-C}} = 44.9$ Hz, P- CH_2), 127.20 (d, $^3J_{\text{P-C}} = 11.5$ Hz, S- $\text{CH}_2\text{-C=}$), 128.55 (d, $^2J_{\text{P-C}} = 12.6$ Hz, C meta), 130.81 (d, $^2J_{\text{P-C}} = 12.6$ Hz, P- $\text{CH}_2\text{-C=}$), 131.64 (d, $^3J_{\text{P-C}} = 10.4$ Hz, C ortho), 131.95 (s, C para), 134.75 (d, $^1J_{\text{P-C}} = 78.3$ Hz, C ipso). EIMS: m/z 254 (M^+ , 33%).

Synthesis of Phenylmethylphosphinous Acid Molybdenumpentacarbonyl Complex 7. To a solution of complex 2 (100 mg, 0.2×10^{-3} mol) in THF (2 mL) at -78 $^\circ\text{C}$ was added dropwise a solution of $t\text{-BuOK}$ (112 mg, 1×10^{-3} mol) in THF (3 mL). The mixture was stirred during 30 min at -78 $^\circ\text{C}$, then CH_3I (142 mg, 1×10^{-3} mol) was added dropwise. The solution was then allowed to warm to room temperature and stirred for 30 min. A singlet at 148.8 ppm was observed on the ^{31}P NMR spectrum. After evaporation, the residue was chromatographed on silica gel with dichloromethane as the eluent. The product was thus obtained as white crystals in 9.3% yield (7 mg). Dimethylnaphthalene was also recovered as white crystals in 51% yield (16 mg) and identified by ^1H NMR, ^{13}C NMR, and mass spectrometry. ^{31}P NMR (CDCl_3): δ 130.63. ^1H NMR (CDCl_3): δ 1.95 (d, 3H, $^2J_{\text{P-H}} = 5.3$ Hz, PCH₃), 3.19 (br s, 1H, OH), 7.45 (m, C_6H_5). ^{13}C NMR (CDCl_3): δ 27.20 (d, $^1J_{\text{P-C}} = 23.0$ Hz, P- CH_3), 127.69 (d, $^2J_{\text{P-C}} = 13.8$ Hz, C meta), 128.95 (d, $^3J_{\text{P-C}} = 10.4$ Hz, C ortho), 130.48 (s, C para), 205.30 (d, $^2J_{\text{P-C}} = 10.4$ Hz, CO cis).

X-ray Structure Characterizations of 2 and 6. Measurements were carried out using a low-temperature device

respectively at $T = 223(2)$ K for 2 and $T = 100(2)$ K for 6 on a Bruker X8 APEX¹⁵ KAPPA-CCD X-ray diffractometer system (Mo radiation, $\lambda = 0.71073$ Å). The automated strategy determination program COSMO¹⁶ was used to define diffraction experiments on the basis of phi and omega scans. Frames were integrated using the Bruker SAINT version 7.06A software¹⁷ and using a narrow-frame integration algorithm.

The integrated frames yielded for 2 a total of 17 501 reflections collected at a maximum 2θ angle of 63.24° (0.68 Å resolution, 6642 independent reflections, $R_{\text{int}} = 0.0386$, $R_{\text{sig}} = 0.0387$, completeness = 88.8%), and 5727 (86.22%) reflections were found greater than $2\sigma(I)$. The unit cell parameters were $a = 9.122(5)$ Å, $b = 9.217(5)$ Å, $c = 14.069(8)$ Å, $\alpha = 102.467(12)^\circ$, $\beta = 95.424(13)^\circ$, $\gamma = 103.508(12)^\circ$, $V = 1109.8(11)$ Å³, $Z = 2$, calculated density $D_c = 1.497$ Mg/m³.

The integrated frames yielded for 6 a total of 21 187 reflections collected at a maximum 2θ angle of 73.64° (0.59 Å resolution, 5439 independent reflections, $R_{\text{int}} = 0.0247$, $R_{\text{sig}} = 0.0191$, completeness = 86.4%), and 5073 (93.27%) reflections were found greater than $2\sigma(I)$. The unit cell parameters were $a = 11.5733(12)$ Å, $b = 6.8944(7)$ Å, $c = 15.7794(16)$ Å, $\alpha = 90.0^\circ$, $\beta = 95.682(5)^\circ$, $\gamma = 90.0^\circ$, $V = 1252.9(2)$ Å³, $Z = 4$, calculated density $D_c = 1.348$ Mg/m³.

Absorption corrections were applied for all data using the SADABS program included in the SAINTPLUS software package.¹⁷ Direct methods using the Sir92 program¹⁸ were used for resolution. Direct methods of phase determination, followed by a subsequent difference Fourier map, led to an electron density map from which most of the non-hydrogen atoms were identified in the asymmetric unit. With subsequent isotropic refinement and some Fourier differences synthesis, all non-hydrogen atoms were identified, and atomic coordinates and isotropic and anisotropic displacement parameters of all the non-hydrogen atoms were refined by means of a full matrix least-squares procedure on F^2 , using SHELXTL software.¹⁹ For 2, hydrogen atoms were included in the refinement in calculated positions, riding on the carbons atoms. In the case of compound 6, fractional coordinates of hydrogen atoms were refined. For both, isotropic thermal parameters of H atoms were fixed 20% and 50% higher than Csp² and Csp³ atoms, respectively, to which there were connected, and torsion angles for methyl groups were refined. The refinement converged at $R_1 = 0.0298$, $wR_2 = 0.0726$, with intensity $I > 2\sigma(I)$, and largest peak/hole in the final difference map were found to be 0.674 and -0.260 e Å⁻³ for 2. $R_1 = 0.0220$, $wR_2 = 0.0623$, with intensity $I > 2\sigma(I)$, and largest peak/hole in the final difference map were found to be 0.596 and -0.270 e Å⁻³ for 6. Drawings of molecules were made using ORTEP32.²⁰

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Supporting Information Available: X-ray crystal structure analysis of compounds 2 and 6. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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