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Metal-Directed Synthesis of Complexes Featuring Functional P,C-Cage Ligands: What Are the Intermediates?

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Thermal reactions of 2*H*-azaphosphirene metal complexes **1a**,**b** (M = W, Mo) with acetylene ethylcarboxylate led to complexes **5** and **8**, which present two different P,C-cage ligands, thus showing a surprising effect of metal-directed synthesis. DFT studies of $[(OC)_5MPC_5Me_5)]$ (M = W, Mo) did not yield the expected ground-state structure as implied by the formula; instead complexes having three isomeric ligand structures (**2′, 10**, **11**) were obtained, one with a zwitterionic structure (**10**). These results, combined with calculations of compliance constants, led to a proposal for the first reaction step that is responsible for the metal-mediation of the reaction course.

Introduction

Metal-directed synthesis is an important and well-established concept in organometallic and coordination chemistry.[1] Although synthesis of P,C-cage heterocycles has received great attention, e.g., via metal atom/*t*-BuCP co-condensation,[2,3] the formation of cages with P−P bonds was a long-standing problem.[4] In the meantime a large variety of structural motifs with P−P bonds are known, e.g., **I**,[5] **II**,[3] and **III**[6] (Figure 1), but the access to *C*-functional P,C-cages having P−P bonds remains difficult. This is mainly because the phosphaalkynes that could deliver the functionality are largely unknown and metal atom/*t*-BuCP/alkyne co-condensation is much less well developed. Therefore, knowledge of valuable synthetic routes to *C*-functional P,C-cage ligands is scarce. One example, BABAR-Phos,[7] has found application in catalysis. The stability of this phosphirane derivative has been attributed to the incorporation of the PC_2 ring into a polycyclic framework, which results in a small sum of bond angles (247°) at phosphorus.

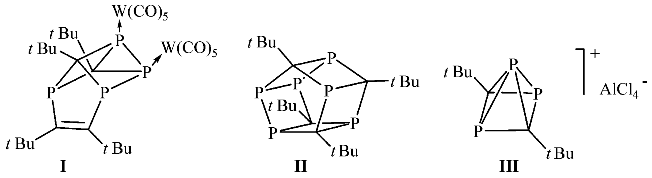

Figure 1. Examples of P,C-cage compounds with P−P bonds.

Recently, we continued our studies[8] on thermal reactions of the 2*H*-azaphosphirene tungsten complex **1a** with alkynes and observed 1*H*-phosphirene complex formation in the first step[8,9] and, as previously, assumed transient formation of the electrophilic terminal phosphinidene tungsten complex **2a** (cf. Scheme 1).

Experimental Results

Here, we report on a comparative experimental study of thermal reactions of 2*H*-azaphosphirene complexes **1a**[10] and **1b**[11] with acetylene ethylcarboxylate (**3**) and, in addition, DFT calculations on potential intermediates. Whereas reaction of complex **1a** selectively furnished complex **5** (**4**[8] via ^{31}P NMR spectroscopically detected), complex **1b** yielded complex **8** (Scheme 1). The first result was as expected and is very reminiscent of the case in which DMAD was used as trapping reagent.[9] However, the second outcome provides evidence for

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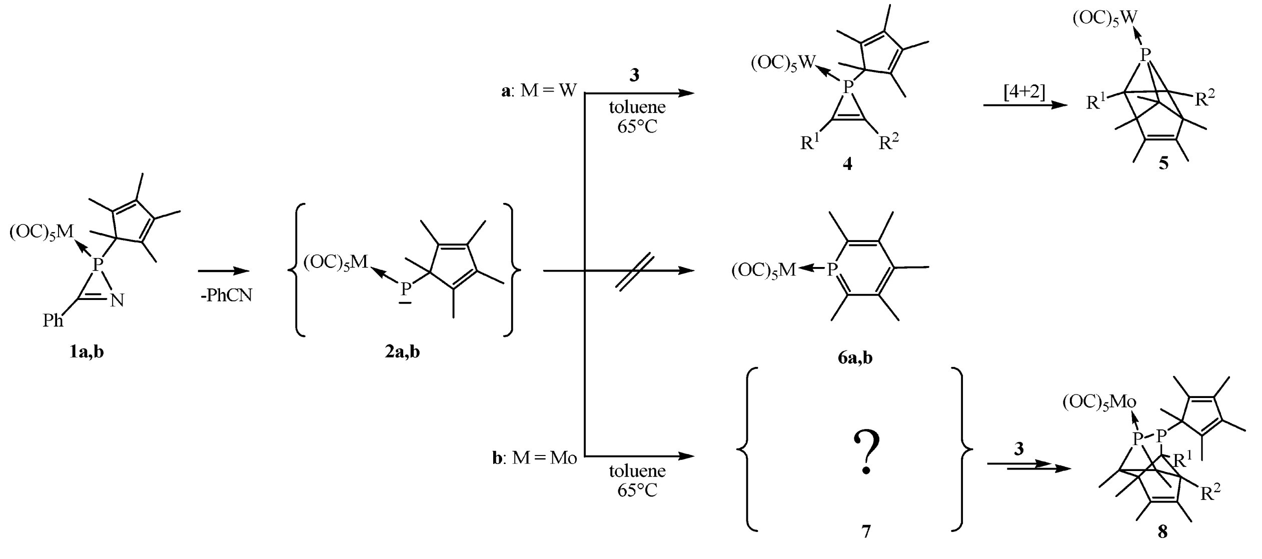
Scheme 1. Proposed Reaction Course of the Thermal Reaction of Complexes 1a,b with Acetylene Ethylcarboxylate (3: $R^1 = H$, $R^2 = CO_2Et$)



an unusual new pathway.[12] Complexes **5** and **8** were structurally established unambiguously by multinuclear NMR studies, mass spectrometry, and elemental analyses and, in addition, complex **8** by single-crystal X-ray analysis.

The $^{31}P\{^1H\}$ NMR investigations showed that complex **4** was intermediately formed in the first case (δ −129.9 ppm), whereas in the other case no intermediates were observed. Both P,C-cage ligands can easily be distinguished by NMR spectroscopy. Because of the significantly different environment of the phosphorus nuclei of the phosphirane moieties in complexes **5** and **8**, the $^{31}P\{^1H\}$ resonance of **5** was observed at −88.5 ppm with a ^1J(W,P) coupling constant magnitude of 231.1 Hz, while the corresponding $^{31}P\{^1H\}$ resonances of complex **8** were found at −106.3 ppm ($^1J(P,P) = 325.7$ Hz) and 23.4 ppm ($^1J(P,P) = 325.7$ Hz). The methylidine moieties also showed substantially different NMR parameters: a ^1H resonance at 2.82 (d, $J(P,H) = 4.8$ Hz) was observed for complex **5** and at 2.38 (dd, $J(P,H) = 19.3$ Hz, $J(P,H) = 11.4$ Hz) for complex **8**.

As the $^{31}P\{^1H\}$ NMR reaction monitoring furnished no information about the reaction course in the case of **1b**, we can only speculate at this point. The more complicated structure of the P,C-cage, together with the "curious" position of the ester group, seems to exclude the formation of a 1*H*-phosphirene complex in the first step.[13] Formation of phosphinine complexes **6a**,**b**—as plausible isomeric structures of **2a**,**b**—was not observed but can be ruled out, at least for **2a**, as no other product was observed besides **4** and **5**. If a very rapid transformation of **6a** had taken place and thus precluded detection, then the final product should have been detected. On the other hand, if the tungsten complex **2a** does not rearrange to **6a**, then there is no reason why **2b** should do. Because of this somewhat confusing outcome, we decided to reexamine the intermediacy of the assumed transient phosphinidene complexes [$(OC)_5MPC_5Me_5$] (**2a**, M = W; **2b**, M = Mo) by computational means (see next section).

The molecular structure of complex **8** was determined by single-crystal X-ray diffraction analysis (Figure 2). Surprisingly, the novel P,C-cage has an only slightly distorted "C_s symmetric" skeleton; that is, opposite bonds such as C6−C11 (1.553(3) Å) and C7−C8 (1.556(3) Å) are identical within the margins of error, as are angles such as C6−C11−C12 (100.4(2)°) and C7−C8−C12 (100.4(2)°) or P1−C6−C11 (114.2(2)°) and P1−C7−C8 (114.4(2)°) (Figure 2); the P1−P2 distance is surprisingly short.[14]

Theoretical Approach

Because of the puzzling situation regarding the intermediates, we performed DFT calculations[15] (B3LYP/6-311g(d,p)/LanL2DZ (at Mo and W))[16] on the structures of **2a**,**b**. Our starting point was the calculation of the binuclear phosphinidene complex [$\{(OC)_5Mo\}_2PC_5Me_5$] (**9**, Figure 3), published by Jutzi et al. some years ago.[17] Virtual removal of either of the $Mo(CO)_5$ fragments yields two possible isomeric complexes with a C_5Me_5 ring σ-bound to phosphorus as candidates for the ground-state structure of [$(OC)_5MoPC_5Me_5$] (**2b**). Surprisingly, instead of these expected geometries, isomers **10b**, **2b′**, and **11b** were obtained as local minima, with **2b′** as the most stable complex within this series and with a close resemblance to assumed structure **2b**, as the two P−C bonds are very long

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[12] Comments: Reactions of complexes **1a**,**b** with alkene derivatives yielded the expected *P*-Cp*-substituted phosphirane complexes, and no transformation of the Cp* group was observed: Bode, M.; von Frantzius, G.; Nieger, M.; Streubel, R. To be published.

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[14] Crystal structure determination of **8**, $C_{30}H_{36}MoO_7P_2$. *Crystal data*: triclinic, space group $P\bar{1}$, $a = 10.4632(11)$ Å, $b = 11.4976(11)$ Å, $c = 13.7306(12)$ Å, $\alpha = 77.195(4)°$, $\beta = 83.751(4)°$, $\gamma = 76.866(4)°$, $U = 1565.6(3)$ Å^3, $Z = 2$, $T = 133$ K. *Data collection*: a crystal ca. 0.14 × 0.13 × 0.07 mm was used to register 27 972 intensities (Mo Kα radiation, $2\theta_{max}$ 60°) on a Bruker SMART 1000 CCD diffractometer. An absorption correction was performed with SADABS. *Structure refinement*: the structure was refined by full-matrix least-squares on F^2 (program SHELXL-97) to wR_2 0.0776, R_1 0.0398 for 372 parameters, 327 restraints (to displacement parameters of the light atoms) and 9106 independent reflections. Hydrogen atoms were included using a riding model or rigid methyl groups.

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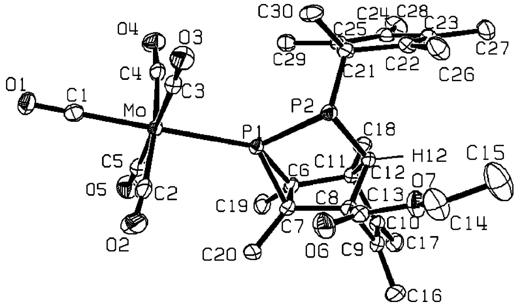

Figure 2. Molecular structure of **8** in the crystal (thermal ellipsoids at 50% probability level; H atoms (except H12) are omitted for clarity). Selected bond lengths (Å) and angles (deg): P1−Mo 2.538(6), P1−P2 2.1848(9), P2−C21 1.892(2), P2−C12 1.855(2), P1−C6 1.876(2), P1−C7 1.875(2), C6−C7 1.524(3), $\sum\angle P^1R_3$ 238(±1)°, $\sum\angle P^2R_3$ 314(±1)°.

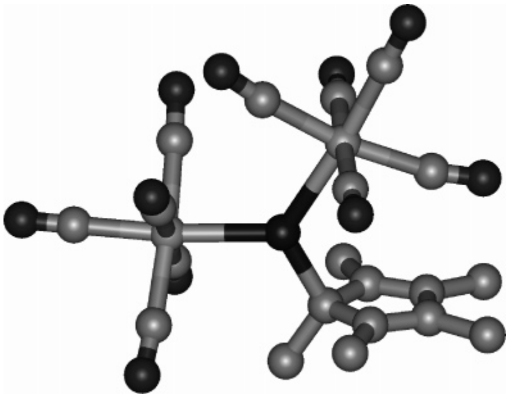

Figure 3. Calculated molecular structure (gas phase) of $[\{(OC)_5Mo\}_2PCp^*]$ (**9**). Selected bond lengths (Å) and angles (deg): Mo1−P 2.508, Mo2−P 2.528, P−C 1.920, Mo1−P−Mo2 124.6, Mo1−P−C 116.6, Mo2−P−C 118.8, $\sum\angle P$ 360°.

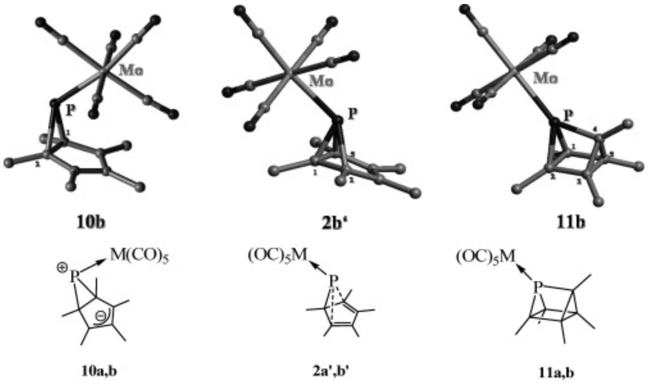

Figure 4. DFT-calculated structures and formulas of $[(OC)_5MPC_5Me_5]$ (M = W, Mo) (**2a**,**b**, **10a**,**b**, and **11a**,**b**). Selected bond lengths (Å) and bond angles (deg) (see also Table 1): **10a**: C1−P−C2 42.5; **2a′**: C1−P−C2 40.0, C2−P−C5 61.7; **11a**: C1−P−C2 48.1, C1−P−C4 75.8, C2−P−C4 75.8; **10b**: C1−P−C2 42.9; **2b′**: C1−P−C2 41.6, C2−P−C5 64.1; **11b**: C1−P−C2 47.9, C1−P−C4 75.6, C2−P−C4 75.6.

(2.155 Å, Figure 4, Table 1). To enable further comparison with the proposed tungsten complex $[(OC)_5WPC_5Me_5]$ (**2a**)—and because we became curious about the structure of the intermediates in this case—we investigated complexes **2a**, **2a′**, **10a**, and **11a**.

Table 1. Relative Stabilities (Δ*G*) of Tungsten Complexes 2a′, 10a, and 11a and Molybdenum Complexes 2b′, 10b, and 11b and Selected Bond Lengths [Å] Thereof

	10		2′		11	
a: M = W						
rel energy[a] (Δ*G* [kJ/mol])	30		0		172	
selected bond lengths [Å]	W−P	2.539	W−P	2.546	W−P	2.538
	P−C1	1.992	P−C1	1.943	P−C1	1.879
	P−C2	2.077	P−C2	2.245	P−C2	1.879
			P−C5	2.245	P−C4	1.899
b: M = Mo						
rel energy[a] (Δ*G* [kJ/mol])	27		0		172	
selected bond lengths [Å]	Mo−P	2.552	Mo−P	2.578	Mo−P	2.559
	P−C1	1.998	P−C1	1.920	P−C1	1.882
	P-C2	2.058	P−C2	2.155	P−C2	1.882
			P−C5	2.155	P−C4	1.900

[a] Zero-point corrected.

Table 2. Bond Lengths [Å] and Compliance Constants [Å/mdyn] of Intermediates 10a/2a′ and 10b/2b′

			M−CO^{tr}		M−CO^{eq}	
M		sym	[Å]	COCO	[Å]	COCO
Mo	**10b**	C_1	2.040	0.463	2.071	0.538
Mo	**2b′**	C_s	2.033	0.460	2.069	0.529
W	**10a**	C_1	2.031	0.388	2.058	0.432
W	**2a′**	C_s	2.032	0.401	2.058	0.434

As the outcome of these calculations was more or less the same as before—with one exception—we will discuss in the following only the structures of the molybdenum complexes. The DFT structure of the P,C-cage moiety of **2b′** (Figure 4) shows one long P−C single bond (P−C1 1.920 Å) and two very long P−C bonds (P−C2 and P−C5 2.155 Å); *the latter are significantly lengthened in the case of* ***2a′*** (P−C2 and P−C5 2.245 Å). In consequence, the bonding of phosphorus to the C_5Me_5 ring might be best described as being between an η^1 and an η^3 coordination mode, being closer to η^1 in the case of **2a′**. With a relative Δ*G* of +27 kJ/mol (Table 1), zwitterionic complex **10b**—with a phosphenium unit and an allyl-anion moiety in the ring—is the next most stable isomer; the ligand structure is highly reminiscent of 4-methylene-6-phosphabicyclo[1.1.0]hex-2-ene, published by Niecke and co-workers in 1996.[18] Interestingly, because of the absence of a symmetry plane, the two P−C bonds in **10b** are inequivalent (1.998 and 2.058 Å), and in addition, they are both longer than the corresponding (equivalent) P−C1 and P−C2 bonds (1.882 Å) in **11b** (the ligand is C_s symmetrical). The latter is significantly higher in energy (+172 kJ/mol), which can be explained by assuming a highly strained P,C-cage ($\sum\angle P$ 200°).

Note that the free ligand (but bearing different substituents) was described by Regitz et al. some years ago.[19] As all of these isomeric potential intermediates—especially **10b** and **2b′**—achieve an additional stabilization of the phosphinidene phosphorus via intramolecular electronic interactions with the π-system of the C_5Me_5 ring,[20] it seems reasonable to assume that one of these complexes is involved in the product formation of **8**.

Assuming now that complexes **2a′**,**b′** are the reactive intermediates, then the reaction courses may differ in the following step. Whereas the tungsten complex **2a′** reacts

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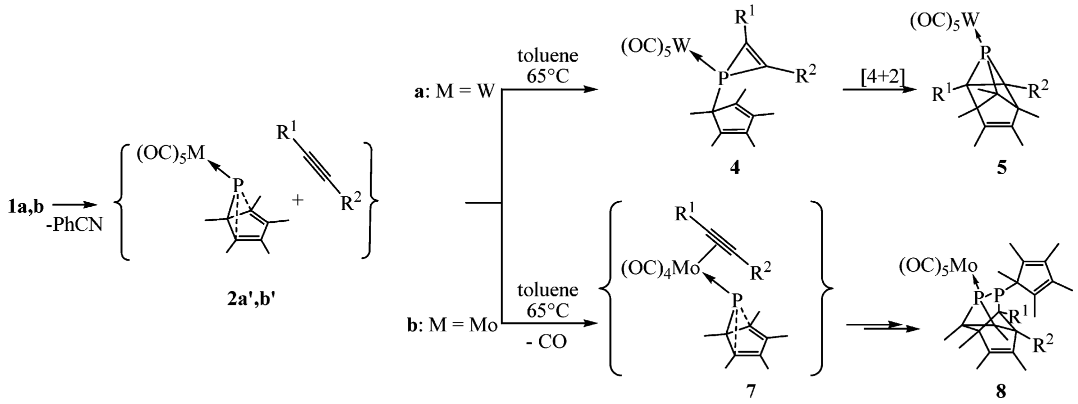
Scheme 2. New Proposal for Reactive Intermediates Involved in Reactions of 1a,b with the Alkyne 3



with the alkyne **3** to yield **4** and then **5**, the molybdenum complex **2b′** might experience loss of CO in the first step and give then the *side*-on coordinated complex **7**, which is transformed into the final product **8** via a multistep process, as yet unknown.

As the first step (CO dissociation) strictly depends on the metal−carbon bond strength, we decided to examine this for the intermediate complexes in question (**10a/2a′** and **10b/2b′**) (Table 2) using the method of compliance constants.[21] The general trend is that equatorial M−CO bonds are longer and more compliant than M−CO trans to the phosphinidene ligand (M = Mo, W), which is interpretable in terms of higher reactivity of equatorial carbonyls toward substitution reactions. Even more important is that a great difference in M−CO^{eq} compliances is induced by the metal, meaning that in molybdenum complexes **10b/2b′** the equatorial M−CO bonds are 20−25% more compliant than those in tungsten complexes **10a/2a′**. These findings lend further support to the proposal shown in Scheme 2.

Further experimental and theoretical studies on reactions of *P*-C$_5$Me$_5$-substituted 2*H*-azaphosphirene chromium, molybdenum, and tungsten complexes with regard to possibly divergent reaction pathways are currently underway. Further DFT calculations will focus on reaction pathways involving reactive species that (might) deliver products in the same way as terminal phosphinidene complexes, but are essentially different in structure and bonding.

Experimental Section

General Procedures. All reactions and manipulations were carried out under an atmosphere of deoxygenated dry nitrogen, using standard Schlenk techniques with conventional glassware, and solvents were dried according to standard procedures. NMR data were collected on a Typ Bruker DPX 200 (295 K), at 81.0 MHz (^{31}P), 50.3 MHz (^{13}C), and 200.1 MHz (^{1}H), using [D$_8$]toluene and [D$_6$]benzene as solvent and internal standard; shifts are given relative to external tetramethylsilane (^{1}H, ^{13}C) and 85% H$_3$PO$_4$ (^{31}P) using TMS and 85% H$_3$PO$_4$ as standard references. Mass spectra were recorded on a Finigan Mat 8430 (70 eV); apart from *m/z* values of the molecule ions, only *m/z* values having intensities of more than 20% are given. Infrared spectra were recorded on a Biorad FT-IR 165 (selected data given). Melting points were obtained on a Büchi 535 capillary apparatus. Elemental analyses were performed using a Elementar (Vario EL) analytical gas chromatograph. All products were separated by column chromatography at low temperature. The *κP* notation in the nomenclature is intended to differentiate between P- and N-coordination of the appropriate heterocycle to the metal.

Synthesis of Complex 5. A 500 mg (0.8 mmol) amount of **1a** and 0.5 mL (5 mmol) of **3** dissolved in 3.5 mL of toluene were stirred at 65 °C for 20 h. The solvent was evaporated and the solid was purified by low-temperature column chromatography to deliver a beige solid, mp 79 °C. Yield: 170 mg (35.0%). Selected NMR data for **5** ([D$_8$]toluene): ^{1}H NMR: 0.21 (d, ^{3}J(P,H) = 19.2 Hz, 3H, CH$_3$), 0.83 (t, ^{3}J(H,H) = 7.1 Hz, 3H, CH$_3$), 1.12 (s, 3H, CH$_3$), 1.21 (m, 3H, CH$_3$), 1.51 (s, 3H, CH$_3$), 1.56 (m, 3H, CH$_3$), 2.82 (d, 1H, *J*(P,H) = 4.8 Hz, PC*H*), 3.77 (dq, 2H, ^{3}J(H,H) = 7.2 Hz, ^{4}J(P,H) = 4.1 Hz, CH$_2$) ppm. ^{13}C{^{1}H} NMR: 6.0 (d, ^{3}J(P,C) = 5.1 Hz, CH$_3$), 10.6 (s, CH$_3$), 11.8 (s, CH$_3$), 13.7 (d, ^{3}J(P,C) = 2.3 Hz, CH$_3$), 14.1 (s, CH$_2$CH$_3$), 15.2 (d, ^{4+4}J(P,C) = 2.6 Hz, CH$_3$), 48.5 (d, ^{2+2}J(P,C) = 11.0 Hz, C$_{cage}$), 49.8 (d, ^{2+2}J(P,C) = 9.6 Hz, C$_{cage}$), 60.5 (s, C$_{cage}$), 68.0 (m, C$_{cage}$ (2×)), 68.9 (d, ^{1}J(P,C) = 33.0 Hz, PC$_{cage}$), 140.3 (d, ^{3+3}J(P,C) = 13.1 Hz, C$_{cage}$), 141.9 (d, ^{3+3}J(P,C) = 10.3 Hz, C$_{cage}$), 169.6 (s, CO$_2$Et), 194.3 (d, ^{2}J(P,C) = 8.0 Hz, *cis*-CO), 197.9 (d, ^{2}J(P,C) = 33.5 Hz, *trans*-CO) ppm. MS (EI, 70 eV): *m/z* = 588 [M$^+$, 28]. Anal. Calcd: C 40.84, H 3.60. Found: C 41.39, H 3.80.

Synthesis of Complex 8. A 200 mg (0.4 mmol) amount of **1b** and 0.2 mL (2 mmol) of **3** dissolved in 1.5 mL of toluene were stirred at 65 °C for 5 h. The solvent was evaporated and the solid was purified by low-temperature column chromatography to deliver a colorless solid, mp 155 °C (dec). Yield: 60 mg (45.0%). Selected NMR data for **8** ([D$_6$]benzene): ^{1}H NMR: 0.73 (s, 3H, CH$_3$), 0.98 (d, 3H, *J*(P,H) = 14.5 Hz, CH$_3$), 1.02 (t, 3H, ^{3}J(H,H) = 7.1 Hz, CH$_3$), 1.27 (s, 3H, CH$_3$), 1.33 (d, 3H, *J*(P,H) = 21.7 Hz, CH$_3$), 1.51−1.55 (m$_c$, 12H, 4× CH$_3$), 1.83 (s, 3H, CH$_3$), 2.10 (s, 3H, CH$_3$), 2.47 (dd, 1H, *J*(P,H) = 19.3 Hz, *J*(P,H) = 11.6 Hz, CH), 4.04 (q, 2H, ^{3}J(H,H) = 7.1 Hz, C*H*$_2$CH$_3$) ppm. ^{13}C{^{1}H} NMR: 8.4 (dd, *J*(P,C) = 9.1 Hz, *J*(P,C) = 2.6 Hz, CH$_3$), 9.6 (d, *J*(P,C) = 12.0 Hz, CH$_3$), 9.7 (s, CH$_3$), 9.8 (s, CH$_3$), 10.4 (s, CH$_3$), 11.3 (s, CH$_3$), 12.8 (dd, *J*(P,C) = 6.3 Hz, *J*(P,C) = 5.0 Hz, C$_{cage}$-CH$_3$ (2×)), 12.9 (s, CH$_3$), 13.0 (s, CH$_3$), 21.0 (d, *J*(P,C) = 32.3 Hz, Cp*(C1)-CH$_3$), 44.9 (dd, *J*(P,C) = 18.8 Hz, *J*(P,C) = 14.5 Hz, C$_{cage}$), 49.1 (dd, *J*(P,C) = 31.0 Hz, *J*(P,C) = 1.9 Hz, C$_{cage}$), 55.1 (dd, *J*(P,C) = 42.5 Hz, *J*(P,C) = 6.3 Hz, Cp*(C1)), 59.3 (s, OCH$_2$), 64.9 (d, *J*(P,C) = 8.4 Hz, C$_{cage}$), 66.7 (dd, *J*(P,C) = 23.6 Hz, *J*(P,C) = 3.2 Hz, C$_{cage}$), 67.6 (d, *J*(P,C) = 33.0 Hz, PCH), 133.4 (d, *J*(P,C) = 4.5 Hz, C$_{cage}$), 134.1 (s, C$_{cage}$), 134.6 (dd, *J*(P,C) = 6.1 Hz, *J*(P,C) = 2.3 Hz, Cp*), 137.7 (dd, *J*(P,C) = 8.1 Hz, *J*(P,C) = 5.2 Hz, Cp*),

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(21) Compliance constants (diagonal elements of the inverse Hessian) are inversely proportional to bond strengths: the smaller the compliance constant, the less compliant (stronger) the bond. (a) Decius, J. C. *J. Chem. Phys.* **1963**, *38*, 241. (b) Jones, L. H.; Swanson, B. I. *Acc. Chem. Res.* **1976**, *9*, 128. (c) Grunenberg, J.; Streubel, R.; von Frantzius, G.; Marten, W. *J. Chem. Phys.* **2003**, *19*, 165.

139.6 (dd, J(P,C) = 6.8 Hz, J(P,C) = 3.6 Hz, Cp*), 140.7 (dd, J(P,C) = 5.2 Hz, J(P,C) = 2.9 Hz, Cp*), 169.2 (s, CO_2), 204.3 (d, J(P,C) = 9.1 Hz, *cis*-CO), 207.4 (dd, J(P,C) = 29.7 Hz, J(P,C) = 1.6 Hz, *trans*-CO) ppm. MS (EI, 70 eV): m/z = 668 [M^+, 2]. Anal. Calcd: C 54.06, H 5.44. Found: C 53.26, H 5.73.

Supporting Information Available: Crystallographic data of **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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