Synthesis and Reactivity of Semibridging Borylene Complexes

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Reaction of the terminal borylene complexes $[(OC)_5M{=}B{=}N(SiMe_3)_2]$ (M = Cr, W) with $[M'(PCy_3)]$ (M′ = Pd, Pt) at room temperature led to spontaneous formation of the heterodinuclear complexes $[(OC)_4M(\mu\text{-}CO)\{\mu\text{-}BN(SiMe_3)_2\}M'(PCy_3)_2]$ (M = Cr, M′ = Pd; M = W, M′ = Pd; M = Cr, M′ = Pt) with concomitant liberation of PCy_3. X-ray diffraction studies revealed that the borylene ligand adopts a semibridging position between the two different metal centers, thus establishing a new coordination mode for borylenes and providing further experimental evidence for the theoretically predicted close relationship between BR and CO. After prolonged reaction times the liberated phosphine substitutes the carbonyl group in trans-position to the borylene moiety, forming complexes of the type $[(Cy_3P)(OC)_3M(\mu\text{-}CO)\{\mu\text{-}BN(SiMe_3)_2\}M'(PCy_3)]$ (M = Cr, M′ = Pt; M = W, M′ = Pt; M = W, M′ = Pd). Heating or photolytic activation of $[(OC)_4M(\mu\text{-}CO)\{\mu\text{-}BN(SiMe_3)_2\}Pd(PCy_3)]$ afforded the terminal borylene complexes *trans*-$[(Cy_3P)(OC)_4M{=}BN(SiMe_3)_2]$, which were fully characterized in the case of M = Cr. Structural data of *trans*-$[(Cy_3P)(OC)_4Cr{=}BN(SiMe_3)_2]$ confirm the presence of an enhanced Cr−B π-back-donation imposed by the phosphine ligand in trans-position.

Introduction

Carbonyl complexes constitute a pivotal class of organometallics, which is characterized by an immense structural diversity and potential for applications. Transition-metal carbonyl complexes are common reagents in organometallic synthesis and are widely used as homogeneous and heterogeneous catalysts, for example in hydroformylations and the Monsanto and Fischer−Tropsch processes.[1] The [TM]−CO linkage is a textbook example of the synergic bond between a ligand with good σ-donor and π-acceptor abilities and a metal center. This favorable metal−ligand interaction gives rise to an ample range of coordination modes for CO, including terminal, bridging, semibridging, and triply bridging. While CO can be replaced by many other ligands, the number of neutral isolobal substituents is somewhat restricted to molecules such as N_2,[2] CNR,[3] CS,[4] or CCR_2.[5] Recent progress in the area of transition-metal complexes of boron[6] has put borylenes, B−R, in the focus as another class of ligands closely related to the ubiquitous CO.[7] In contrast to the metastable and readily available carbon oxide, however, borylenes are highly reactive, transient species. They can be generated and observed either at low temperatures in matrices[8] or at high temperatures in the gas phase,[9] but cannot be handled under ambient conditions. In 1995 we obtained $[\{(\eta^5\text{-}C_5H_5)Mn(CO)_2\}_2\{\mu\text{-}BNMe_2\}]$ (**1**) as the first complex in which a transient borylene was generated and stabilized in the coordination sphere of a transition metal,[10] and subsequent theoretical studies revealed that the σ-donating and π-accepting properties of borylenes even exceed those of the isoelectronic CO, thus rationalizing the thermodynamically very stable metal−borylene linkage.[11] In recent years we[12] and others[13] reported on a variety of bridging and terminal borylene complexes,

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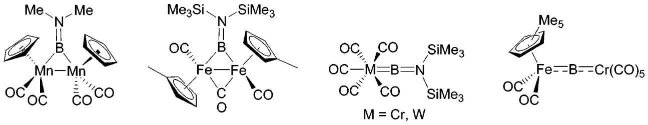
Chart 1. Selected Terminal and Bridging Borylene Complexes



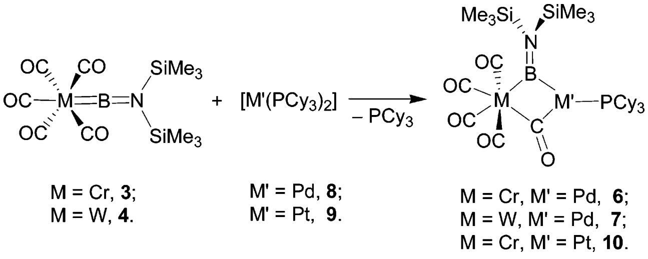
1 **2** **3, 4** **5**

including the species $[\{(\eta^5\text{-}C_5H_4Me)Fe(CO)\}_2(\mu\text{-}CO)\{\mu\text{-}BN(SiMe_3)_2\}]$(**2**),[12a] $[(OC)_5M{=}B{=}N(SiMe_3)_2]$ (M = Cr,[12b] **3**; W,[12b] **4**), and $[(\eta^5\text{-}C_5Me_5)(OC)_2Fe{-}B{=}Cr(CO)_5]$ (**5**).[12e]Introductory reactivity studies on bridging[14] and terminal borylene complexes revealed the propensity of the latter to transfer the B−R ligand to organic[15] substrates and transition metals, thus serving as a unique source of the elusive borylenes under ambient conditions. The successful intermetal−borylene transfer under thermal[16] or, more commonly, photochemical conditions[17] and the pronounced affinity of metal-coordinated boryls[12g,18] and borylenes[19] toward low-valent species of the type $[ML_2]$ (M = Pd, Pt; L = PR_3) prompted us to investigate reactions of complexes of the type $[(OC)_5M{=}B{=}N(SiMe_3)_2]$ (M = Cr, **3**; W, **4**) with suitable Pd^0 species. Recently, we communicated the formation and structure of the first semibridging borylene complexes $[(OC)_4M(\mu\text{-}CO)\{\mu\text{-}BN(SiMe_3)_2\}Pd(PCy_3)_2]$ (M = Cr, **6**; W, **7**) as an, at its time, unprecedented example for the reaction of a terminal borylene complex under thermal conditions.[20]

Here we report full details on the synthesis and structural characterization of a representative range of novel complexes featuring semibridging borylene ligands. Reactivity studies carried out with these species gave access to the first terminal borylene complexes that display a R_3P ligand in trans-position to the borylene, thus providing valuable experimental information about the metal−borylene bonding.

Results and Discussion

Scheme 1. Synthesis of Semibridging Borylene Complexes 6, 7, and 10



Synthesis and Characterization of Heterodinuclear Borylene Complexes with One Phosphine Ligand. To extend the photochemically induced borylene transfer to late transition metals, we choose electron-rich, but coordinatively unsaturated species $[M'(PCy_3)_2]$ (M′ = Pd,[21a] **8**; Pt,[21b] **9**) as potentially useful acceptors for B−R. Interestingly, multinuclear NMR spectra indicated a spontaneous reaction between $[(OC)_5M{=}B{=}N(SiMe_3)_2]$ (M = Cr,[12b,17a] **3**; W,[12b] **4**) and **8** and **9** in C_6D_6 at ambient temperature, without irradiation, furnishing PCy_3 and the new complexes $[(OC)_4M(\mu\text{-}CO)\{\mu\text{-}BN(SiMe_3)_2\}M'(PCy_3)]$ (M = Cr, M′ = Pd, **6**; M = W, M′ = Pd, **7**; M = Cr, M′= Pt, **10**) (Scheme 1).

The ^1H NMR spectra show one singlet for the trimethylsilyl group around $\delta = 0.42$, which is deshielded with respect to that of the borylene precursors ($\delta = 0.12{-}0.14$).[12b,17a] A sharp singlet at $\delta = 10.0$ in the $^{31}P\{^1H\}$ NMR spectra confirms the liberation of one PCy_3 ligand from the Pd and Pt precursors, respectively,[22] and in addition, one signal is found for the metal-coordinated phosphine group ($\delta = 34.2$ (**6**), 41.9 (**7**), 70.0 (**10**)). The new compounds display a broad singlet in the $^{11}B\{^1H\}$ NMR spectra ($\delta = 100$ (**6**), 97 (**7**), 98 (**10**)), which is slightly downfield-shifted with respect to that of the corresponding precursors $[(OC)_5M{=}B{=}N(SiMe_3)_2]$ ($\delta = 92.3$ (**3**), 86.6 (**4**)),[12b,17a] thus indicating the presence of a bridging borylene ligand. To obtain the pure compounds **6**, **7**, and **10**, it is necessary to restrict the time of reaction to a minimum, as the presence of liberated PCy_3 gives rise to subsequent transformations, which are discussed in detail in the following section.

The exact constitution of the new complexes could be determined by performing a single-crystal X-ray diffraction study of **6**.[20] Crystals of **6** were obtained by cooling a concentrated toluene solution to −35 °C; the complex crystallizes in the monoclinic space group $P2_1/n$.In the molecule, the heteronuclear fragments $[(OC)_4Cr]$ and $[PdPCy_3]$ are linked by a borylene and a CO group, which both adopt a semibridging disposition (vide infra). The Cr1−B1 bond (2.0842(18) Å) is approximately 9 pm longer than in the corresponding terminal borylene complex (1.996(6) Å (**3**)),[17a] which is in agreement with the increased coordination number of the boron center in the former. Likewise, the Pd1−B1 bond distance (2.0425(18) Å) corresponds to Pd−B bond distances commonly found in complexes featuring three coordinated boron atoms linked to palladium centers (2.006(9) to 2.077(6) Å).[23] The B1−N1 bond (1.377(2) Å) is only insignificantly longer than in the corresponding borylene complex (1.353(6) Å (**3**)),[17a] thus proving significant double-bond character of the boron−nitrogen linkage.

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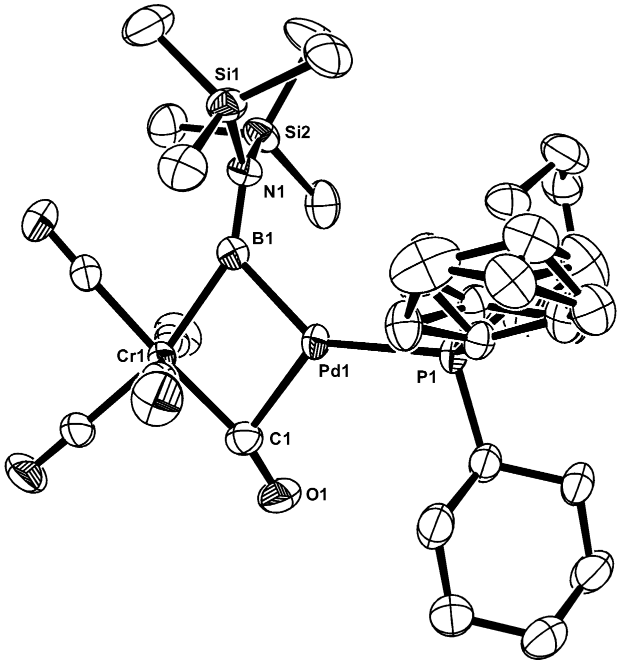

Figure 1. Molecular structure of **6**.

The plane of the bis(trimethylsilyl)amino substituent is orientated almost perpendicular to the plane of the metals and the boron atom (Si1−N1−B1−Pd1: 91.12(15)° (**6**)). This particular arrangement differs from other bridged borylene complexes, e.g., $[\{(\eta^5\text{-}C_5H_5)Mn(CO)_2\}_2\{\mu\text{-}BNMe_2\}]$[10a] (**1**) or $[\{(\eta^5\text{-}C_5H_4Me)Fe(CO)\}_2(\mu\text{-}CO)\{\mu\text{-}BN(SiMe_3)_2\}]$ (**2**),[12a] which comprise formally sp^2-hybridized boron centers. In **1**, the plane of the dimethylamino substituent is almost coplanar (8(3)°) with respect to the Mn_2B plane, and a B−N bond length of 1.39(1) Å indicates a strong B−N π-interaction.[10a] For **2**, however, the Si_2B plane and the Fe_2B plane are twisted by 53(1)°, and the increased B1−N1 distance of 1.412(4) Å is in agreement with a less effective π-interaction between the nitrogen and the boron atom.[12a] Accordingly, in the new compound **6**, the perpendicular orientation of the B- and N-bonding planes should entirely preclude any π-interaction and, thus, impose an even increased B−N separation. Hence, a different bonding situation has to be assumed for the bridged borylene complex **6**, which can be rationalized considering the theoretically predicted similarity between CO and the borylene unit.[24] The Lewis basic palladium fragment donates electron density into the empty π*-orbitals of CO and the π-orbitals of the borylene, and therefore, the electronically saturated $[(OC)_5M{=}B{=}N(SiMe_3)_2]$ acts as a π-acceptor. A partial rehybridization of the carbon and boron centers is necessary to allow for efficient π-acceptance, which results in the formation of two noncompensating, semibridging ligands: CO and $BN(SiMe_3)_2$. In the case of the carbonyl group the relevant bonding angles (Pd1−Cr1−C1: 54.21(6)°, Cr1−C1−O1: 165.49(16)°) are consistent with the classification scheme for semibridging carbonyl ligands developed by Crabtree.[25] For borylenes, no literature data are accessible for semibridging B−R moieties, but the angles (Pd1−Cr1−B1: 49.84(5)°, Cr1−B1−N1: 152.33(13)°) lie clearly between those typically found for terminal and symmetrically bridging ligands. Preliminary ELF calculations suggest the absence of a metal−metal interaction, despite the relatively small chromium−palladium distance of 2.6227(10) Å.

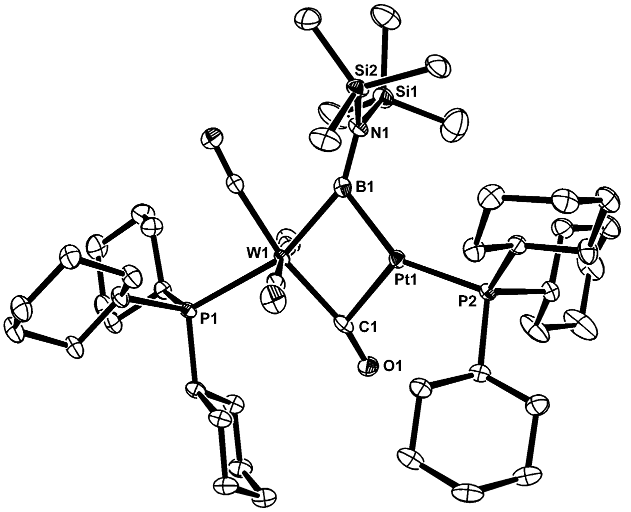

Figure 2. Molecular structure of **11**.

Synthesis and Characterization of Heterodinuclear Borylene Complexes with Two Phosphine Ligands. To complete the series of new compounds with respect to combinations of W with Pt, $[(OC)_5W{=}B{=}N(SiMe_3)_2]$ (**5**) was reacted with $[Pt(PCy_3)_2]$ (**9**) in C_6D_6 under identical conditions. Surprisingly, however, multinuclear NMR data proved the spontaneous formation of a different type of product, namely, $[(Cy_3P)(OC)_3W(\mu\text{-}CO)\{\mu\text{-}BN(SiMe_3)_2\}Pt(PCy_3)]$ (**11**). The $^{31}P\{^1H\}$ NMR spectrum displayed two doublets ($\delta = 76.8$ (d, $^4J_{P-P} = 10$ Hz, $^1J_{P-Pt} = 5001$ Hz, P_{Pt}), 29.0 (d, $^4J_{P-P} = 10$ Hz, $^1J_{P-W} = 243$ Hz, P_W)), indicating the presence of two nonequivalent phosphine ligands. The singlet for the Me_3Si groups in the ^1H NMR spectra ($\delta = 0.64$) and the broad resonance in the $^{11}B\{^1H\}$ NMR spectra ($\delta = 99$) were found downfield-shifted with respect to the signals of the starting material.[12b]

The molecular constitution of the new compound could be determined by an X-ray diffraction study of a single crystal of **11**. Crystals were obtained be layering hexanes on a concentrated solution of **11** and allowing the solvent to evaporate slowly.The structural features of **11** in particular with respect to the geometries of the CO (Pt1−W1−C1: 51.37(8)°, W1−C1−O1: 165.7(2)°) and the borylene ligand (Pt1−W1−B1: 49.40(9)°, W1−B1−N1: 153.4(2)°) resemble those of the monophosphine Pd complex **6**. These data together with the orthogonal disposition of the aminoborylene with respect to the M−B−Pt plane (Si2−N1−B1−W1: 93.4(5)°) and the short B−N double bond (B1−N1 = 1.407(4) Å) unambiguously prove the presence of semibridging borylene and CO ligands, respectively. Inspection of the W−B distance, however, reveals a distinct difference between the mono- and diphosphine complexes. In the case of **11**, the W1−B1 distance of 2.138(3) Å is shorter than that in the terminal tungsten borylene complex **4** (W−B: 2.151(7) Å),[12b] despite the greater coordination number of the boron atom in the former. Apparently, the decreased W−B distance in **11** is due to the presence of the PCy_3 group in trans-position and its reduced π-acceptor abilities in comparison to CO, thus inducing a stronger M−B $d_\pi - p_\pi$ back-donation. A similar effect is observed in the case of terminal borylene complexes with Cy_3P ligands in trans-position to the boron atom (vide infra). Despite the relatively short tungsten−platinum distance of 2.70833(16) Å, preliminary ELF calculations provide no evidence for a metal−metal interaction.

The formation of the Pt diphosphine complex **11** is obviously due to the presence of free PCy_3 in the reaction mixture, and the selective substitution of a CO ligand trans to the BR_2 group

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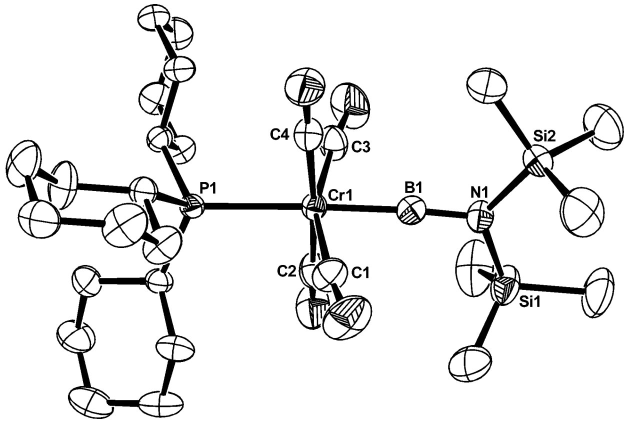
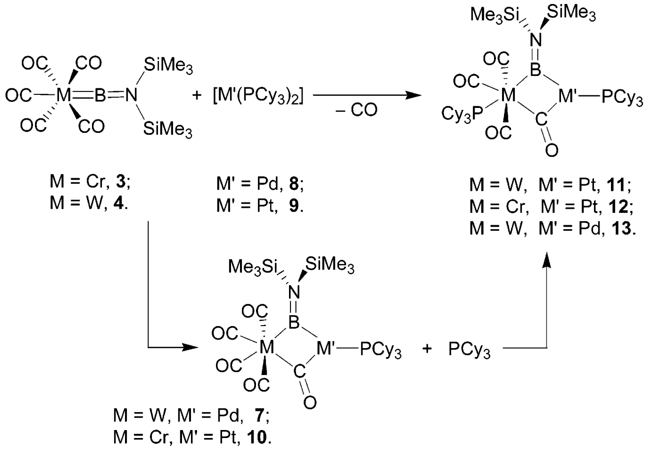


Figure 3. Molecular structure of **14**.

Scheme 2. Synthesis of Semibridging Borylene Complexes with Two Phosphine Ligands



can be explained by the strong trans effect of the latter.[26] The isolation and full spectroscopic characterization of the complex $[(Cy_3P)(OC)_3Cr(\mu\text{-}CO)\{\mu\text{-}BN(SiMe_3)_2\}Pt(PCy_3)]$ (**12**) provide further evidence for this assumed course of the reaction. After separation of deposited, crystalline $[(OC)_4Cr(\mu\text{-}CO)\{\mu\text{-}BN(SiMe_3)_2\}Pt(PCy_3)]$ (**10**) from its reaction mixture, the resulting mother liquor contained dissolved **10** and free PCy_3 according to ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. Over a period of 2 days these species were gradually consumed and the diphospine complex **12** was formed as indicated by corresponding resonances in the ^1H ($\delta = 0.63$), $^{11}B\{^1H\}$ ($\delta = 97$), and $^{31}P\{^1H\}$ ($\delta = 63.9$, $^3J_{P-Pt} = 127$ Hz; 70.1, $^1J_{P-Pt} = 4972$ Hz) NMR spectra. Likewise, 1:1 mixtures of $[(OC)_5W{=}B{=}N(SiMe_3)_2]$ (**4**) and $[Pd(PCy_3)]$ (**8**), from which the monophosphine complex $[(OC)_4W(\mu\text{-}CO)\{\mu\text{-}BN(SiMe_3)_2\}Pd(PCy_3)]$ (**7**) was isolated after 1 day (vide supra), afforded the diphosphine species $[(Cy_3P)(OC)_3W(\mu\text{-}CO)\{\mu\text{-}BN(SiMe_3)_2\}Pd(PCy_3)]$ (**13**) after prolonged time at ambient temperature. **13** was isolated as orange crystals in analytically pure form and displays a broad signal at $\delta = 98$ in the $^{11}B\{^1H\}$ NMR spectrum and two doublets at $\delta = 39.7$ ($^4J_{P-P} = 11$ Hz) and 30.8 ($^4J_{P-P} = 11$ Hz) in the $^{31}P\{^1H\}$ NMR spectra.

Reactivity. The color of solid samples of the bridged borylene complexes **6**, **7**, and **10**−**13** ranges from yellow to red, with the chromium complexes displaying the least intense color with respect to their tungsten congeners. All new compounds proved to be air and moisture sensitive and thermolabile in solution. In the case of **6**, multinuclear NMR spectra of a solution in C_6D_6 indicated the formation of a new compound with concomitant darkening of the NMR sample, which proceeds very slowly at ambient temperature, but is completed after 1 day at 80 °C. Photolysis of **6** furnishes the same product within 4 h with concomitant formation of a black deposit. The observed singlets in the ^1H NMR ($\delta = 0.38$), $^{11}B\{^1H\}$ NMR ($\delta = 94$), and $^{31}P\{^1H\}$ NMR spectra ($\delta = 64.77$) clearly indicate that **6** is converted into *trans*-$[(Cy_3P)(OC)_4Cr{=}BN(SiMe_3)_2]$ (**14**) with migration of the PCy_3 ligand from Pd to Cr, formation of Pd^0, and release of one CO group. Compound **14** could be isolated after repeated recrystallization steps as yellow crystals. The fact that the substitution occurs selectively in position trans to the borylene ligand is ascribed to the strong trans effect of the latter.

The constitution of the new compound **14** could be determined by performing a single-crystal X-ray diffraction study. Suitable crystals were obtained by cooling a concentrated hexane solution of **14** to −35 °C.The complex crystallizes in the monoclinic space group $P2_1/c$, and the P−Cr−B and the Cr−B−N moieties are almost linearly arranged (P1−Cr1−B1: 177.87(6)°, Cr1−B1−N1: 175.91(16)°). The B1−N1 bond (1.364(3) Å) is negligibly longer than the B1−N1 bond of the unsubstituted borylene **3** (1.353(6) Å),[17a] but the Cr1−B1 bond (1.915(2) Å) is 8.1 pm shorter (1.996(6) Å).[17a] The latter can be rationalized, considering the different electronic situation imposed by the phosphine ligand in trans-position. Being a much less effective π-acceptor with respect to CO, the Cy_3P ligand allows for a stronger $d_\pi - p_\pi$ back-bonding to boron, which leads to a significant decrease of the Cr−B separation. Consequently,[27] a more pronounced umbrella effect is detectible for **14** with respect to the unsubstituted borylene complex **3**, as expressed by the mean values of $B-M-C_{eq}$ and $M-C_{eq}-O$ angles for the C1−O1 and C3−O3 carbonyls (**14**: B1−Cr1−C(1,3): 79°, Cr1−C(1,3)−O(1,3): 174°; **3**: $B-Cr-C_{eq}$: 88°, $Cr-C_{eq}-O$: 179°).[17a] It should be noted that the Si_2NB plane in **14** is almost coplanar with respect to the C2−Cr1−C4 plane (Si1−N1−Cr1−C2: 11.46°, Si2−N1−Cr1−C4: −1.99°), thus precluding a corresponding bending of the C2−O2 and C4−O4 carbonyl ligands toward the borylene for sterical reasons (B1−Cr1−C(2,4): 92°, Cr1−C(2,4)−O(2,4): 178°). All relevant structural data indicate a significantly enhanced Cr−B π-back-bonding in **14**, thus emphasizing its importance for the synergic metal−boron bonding even in the case of aminoborylene complexes, in which the electron deficiency of the boron center is already partially saturated by the presence of a B−N double bond.

Likewise, warming or irradiation of the tungsten species **7** led to the mononuclear phosphine complex *trans*-$[(Cy_3P)(OC)_4W{=}BN(SiMe_3)_2]$ (**15**) as indicated by its characteristic ^1H NMR ($\delta = 0.38$), $^{11}B\{^1H\}$ NMR ($\delta = 90$), and $^{31}P\{^1H\}$ NMR ($\delta = 35.1$) data. In contrast to the clean synthesis of **14** according to Scheme 3, however, the formation of compound **15** is accompanied by various, mostly unidentified side products, thus precluding its isolation in pure form. Among the latter, the boron-free species $[(Cy_3P)W(CO)_5]$ ($^{31}P\{^1H\}$ $\delta = 32.3$)[28] and the aforementioned diphosphine complex $[(Cy_3P)(OC)_3W(\mu\text{-}CO)\{\mu\text{-}BN(SiMe_3)_2\}Pd(PCy_3)]$ (**13**: $^{31}P\{^1H\}$ $\delta = 39.8$ (d), 30.8 (d)) were unambiguously identified by their characteristic $^{31}P\{^1H\}$ NMR resonances. It should be noted that the synthesis of the dinuclear Pt species $[(OC)_4Cr(\mu\text{-}CO)\{\mu\text{-}BN(SiMe_3)_2\}Pt(PCy_3)]$ (**10**) and $[(Cy_3P)(OC)_3M(\mu\text{-}CO)\{\mu\text{-}BN(SiMe_3)_2\}Pt\text{-}$

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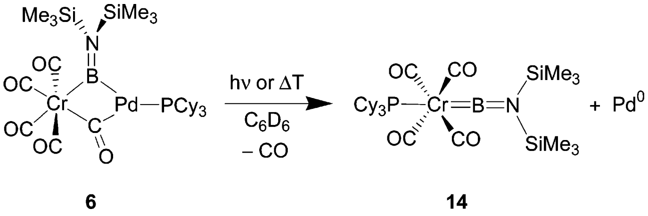
(26) (a) Zhu, J.; Lin, Z.; Marder, T. B. *Inorg. Chem.* **2005**, *44*, 9384−9390. (b) Sakaki, S.; Kai, S.; Sugimoto, M. *Organometallics* **1999**, *18*, 4825−4837.

(27) Uddin, J.; Boehme, C.; Frenking, G. *Organometallics* **2000**, *19*, 571−582.

(28) Demircan, O.; Özkar, S.; Ülkü, D.; Yildirim, L. T. J. *Organomet. Chem.* **2003**, *688*, 68−74.

Scheme 3. Formation of a Phosphine-Substituted Borylene Complex



(PCy$_3$)] (M = Cr, **12**; W, **11**) according to Schemes 1 and 2 under moderate thermal conditions (i.e., ambient temperature) is also accompanied by the formation of similar side products, thus accounting for the observed moderate yields of the isolated pure products. In the case of the reaction of **4** with **9** for example, NMR data recorded 1 h after mixing of the reactants indicate **11** as the major product. After 1 day a 3:2:1:1 mixture of the subsequently isolated product **11**, the borylene complex **15**, [(Cy$_3$P)W(CO)$_5$], and *trans*-[(Cy$_3$P)$_2$W(CO)$_4$] (^{31}P{^{1}H} δ = 31.4 ppm) was observed.[28]

Interestingly, the formation of *trans*-[(Cy$_3$P)(OC)$_4$Cr=BN(SiMe$_3$)$_2$] (**14**) from the dinuclear species **6** represents the only access to substituted terminal borylene complexes, as earlier attempts to obtain mixed phosphine borylene complexes by direct reaction of **3** with PR$_3$ met with no success.[29]

Conclusion

Reaction of the terminal borylene complexes [(OC)$_5$M=B=N(SiMe$_3$)$_2$] (M = Cr, **3**; W, **4**) with [M′(PCy$_3$)$_2$] (M′ = Pd, **8**; Pt, **9**) led to a variety of heterodinuclear, semibridging borylene complexes of the type [(OC)$_4$M(μ-CO){μ-BN(SiMe$_3$)$_2$}M′(PCy$_3$)] (M = Cr, M′ = Pd, **6**; M = W, M′ = Pd, **7**; M = Cr, M′ = Pt, **10**) with liberation of free PCy$_3$. The trans effect of the bridging borylene facilitates the subsequent substitution of a Cr- or W-bound CO by PCy$_3$, which gave access to several diphosphine complexes, [(Cy$_3$P)(OC)$_3$M(μ-CO){μ-BN(SiMe$_3$)$_2$}M′(PCy$_3$)] (M = Cr, M′ = Pt, **12**; M = W, M′ = Pd, **13**; M = W, M′ = Pt, **11**). Structural characterization of [(Cy$_3$P)(OC)$_3$W(μ-CO){μ-BN(SiMe$_3$)$_2$}Pt(PCy$_3$)] (**11**) has confirmed the presence of not only a semibridging borylene but also a decreased W−B distance, imposed by the weak π-acceptor PCy$_3$ in trans-position to the borylene. Likewise, in *trans*-[(Cy$_3$P)(OC)$_4$Cr=BN(SiMe$_3$)$_2$] (**14**), which was obtained by photolysis from [(OC)$_4$Cr(μ-CO){μ-BN(SiMe$_3$)$_2$}Pd(PCy$_3$)] (**6**) as the first terminal borylene complex with a heteroleptic set of neutral co-ligands, the phosphine imposes a significantly enhanced Cr−B d$_\pi$−p$_\pi$ back-bonding. The assembled experimental data establish the semibridging coordination mode as an alternative for the binding of borylenes to transition metals, thus emphasizing the close relationship between BR and CO. Furthermore, the first structural data on bridging and terminal borylene complexes with a PR$_3$ co-ligand in trans-position stress the significance of the π-contribution to the net synergic M−B bonding even in the case of aminoborylenes, for which the electron deficiency of the boron center is already partially saturated by the presence of a B−N double bond.

Experimental Section

General Procedures. All manipulations were conducted either under an atmosphere of dry argon or in vacuo using standard Schlenk line or glovebox techniques. Solvents were dried by standard methods and were distilled from appropriate drying agents (sodium and sodium wire) under dry argon and stored over molecular sieves prior to use. Deuterated solvents (C$_6$D$_6$) were degassed by three freeze−pump−thaw cycles and stored over molecular sieves in the glovebox. The irradiation experiments were carried out through use of a Heraeus TQ 150 high-pressure Hg lamp. IR spectra for compounds were recorded as toluene solutions between KBr plates on a Bruker Vector 22 FT-IR spectrometer. NMR spectra were recorded on Bruker DRX 300, Bruker AMX 400, and Bruker Avance 500 NMR spectrometers. Reaction mixtures were controlled on a Varian 200 NMR spectrometer. ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced to external TMS via the residual protio solvent (^{1}H) or the solvent itself (^{13}C). ^{11}B{^{1}H} and ^{31}P{^{1}H} NMR spectra were referenced to external BF$_3$·OEt$_2$ and 85% H$_3$PO$_4$, respectively. Microanalyses for C, H, and N were performed by Mr. C. P. Kneis (University of Würzburg) on a Leco CHNS-932 instrument.

Synthesis of [(OC)$_4$Cr(μ-CO)(μ-BN(SiMe$_3$)$_2$)Pd(PCy$_3$)] (6). A pale yellow solution of **8** (0.276 g, 0.413 mmol) in toluene (4 mL) was added to solid **3** (0.150 g, 0.413 mmol). Yellow crystals started to form from the bright yellow solution at room temperature. The crystallization was completed at −35 °C, yielding 0.249 g of **6** (81%). ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C, TMS): δ 1.94−1.13 (m, 33 H, Cy), 0.42 (s, 18 H, SiMe$_3$). ^{13}C{^{1}H} NMR (101 MHz, C$_6$D$_6$, 25 °C): δ 223.5 (d, $J_{\text{C-P}}$ = 2 Hz, CO), 223.0 (d, $J_{\text{C-P}}$ = 3 Hz, CO), 33.7 (d, $^1J_{\text{C-P}}$ = 14 Hz, C$_1$, Cy), 31.4 (d, $^3J_{\text{C-P}}$ = 6 Hz, C$_{3,5}$, Cy), 27.7 (d, $^2J_{\text{C-P}}$ = 11 Hz, C$_{2,6}$, Cy), 26.4 (s, C$_4$, Cy), 3.7 (s, SiMe$_3$). ^{11}B{^{1}H} (64 MHz, C$_6$D$_6$, 25 °C): δ 100 (s, $\omega_{1/2}$ = 752 Hz). ^{31}P{^{1}H} NMR (162 MHz, C$_6$D$_6$, 25 °C): δ 34.2 (s). IR (toluene): 2030, 1957, 1932, 1858 cm^{-1}, ν (C=O). Anal. Calcd for C$_{29}$H$_{51}$NBCrO$_5$PPdSi$_2$: C 46.44, H 6.85, N 1.87. Found: C 46.43, H 6.80, N 1.86.

Synthesis of [(OC)$_4$W(μ-CO)(μ-BN(SiMe$_3$)$_2$)Pd(PCy$_3$)] (7). A pale yellow solution of **8** (0.135 g, 0.202 mmol) in toluene (4 mL) was added to solid **4** (0.100 g, 0.202 mmol). After 24 h the volume of the red solution was reduced to approximately half, and the mixture was cooled to −80 °C. An orange microcrystalline solid of **7** deposited after several days, which was isolated and dried in vacuo (0.120 g, 67%). ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C, TMS): δ 1.96−1.13 (m, 33 H, Cy), 0.42 (s, 18 H, SiMe$_3$). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$, 25 °C): δ 203.1 (d, $^1J_{\text{C-W}}$ = 121 Hz, $J_{\text{C-P}}$ = 2 Hz, CO), 200.5 (d, $J_{\text{C-P}}$ = 3 Hz, CO), 34.0 (d, $^1J_{\text{C-P}}$ = 12 Hz, C$_1$, Cy), 31.4 (d, $^3J_{\text{C-P}}$ = 5 Hz, C$_{3,5}$, Cy), 27.8 (d, $^2J_{\text{C-P}}$ = 11 Hz, C$_{2,6}$, Cy), 26.4 (s, $^4J_{\text{C-P}}$ = 1 Hz, C$_4$, Cy), 3.9 (s, SiMe$_3$). ^{11}B{^{1}H} (96 MHz, C$_6$D$_6$, 25 °C): δ 97 (s, $\omega_{1/2}$ = 884 Hz). ^{31}P{^{1}H} NMR (121 MHz, C$_6$D$_6$, 25 °C): δ 41.9 (s). IR (toluene): 2043, 1955, 1932, 1873 cm^{-1}, ν (C=O). Anal. Calcd for C$_{29}$H$_{51}$NBO$_5$PPdSi$_2$W: C 39.49, H 5.83, N 1.59. Found: C 39.48, H 5.75, N 1.65.

Synthesis of [(OC)$_4$Cr(μ-CO){μ-BN(SiMe$_3$)$_2$}Pt(PCy$_3$)] (10). Solid **3** (0.045 g, 0.124 mmol) was added to a pale yellow solution of **9** (0.094 g, 0.124 mmol) in C$_6$D$_6$ (0.5 mL). The solution turned orange, and after 5 min orange crystals formed. These were separated from the solution and recrystallized from toluene/hexane by slow evaporation in the glovebox. After 4 days orange crystals of **10** could be isolated (yield 0.025 g, 25%). ^{1}H NMR (500 MHz, C$_6$D$_6$, 27 °C): δ 2.00−1.09 (m, 33 H, Cy), 0.43 (s, 18 H, SiMe$_3$). ^{13}C{^{1}H} NMR (126 MHz, C$_6$D$_6$, 27 °C): δ 223.5 (s, CO), 223.3 (d, $J_{\text{C-P}}$ = 2 Hz, CO), 35.8 (d, $^1J_{\text{C-P}}$ = 24 Hz, C$_1$, Cy), 31.0 (s, C$_{3,5}$, Cy), 27.6 (d, $^2J_{\text{C-P}}$ = 11 Hz, C$_{2,6}$, Cy), 26.4 (s, C$_4$, Cy), 3.5 (s, SiMe$_3$). ^{11}B{^{1}H} NMR (160 MHz, C$_6$D$_6$, 27 °C): δ 98 (s, $\omega_{1/2}$ = 1230 Hz). ^{31}P{^{1}H} NMR (202 MHz, C$_6$D$_6$, 27 °C): δ 70.0 (s, $_1J_{\text{P-Pt}}$ = 5134 Hz). IR (toluene): 2029, 1956, 1933, 1858 cm^{-1}, ν (C=O). Anal. Calcd for C$_{29}$H$_{51}$NBCrO$_5$PPtSi$_2$: C 41.53, H 6.13, N 1.67. Found: C 41.22, H 6.05, N 1.64.

Synthesis of [(Cy$_3$P)(OC)$_3$W(μ-CO){μ-BN(SiMe$_3$)$_2$}Pt(PCy$_3$)] (11). Solid **4** (0.050 g, 0.101 mmol) was added to a pale yellow solution of **9** (0.077 g, 0.101 mmol) in toluene (0.5 mL). The

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(29) Kollann, C. Ph.D. Thesis, RWTH Aachen, 1999.

mixture turned brown-red and was layered with hexane (2 mL). The solvent was allowed to evaporate from the reaction mixture in the glovebox. First some side products precipitated, which were removed. The residual red solution was left in the glovebox, and the solvent was allowed to evaporate slowly. After 7 days bright orange crystals of **11** formed, which were recrystallized from toluene/hexane, yielding 30 mg (24%). ^{1}H NMR (400 MHz, C_6D_6 , 27 °C): δ 2.20−1.20 (m, 66H, Cy), 0.64 (s, 18H, SiMe$_3$). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6 , 27 °C): δ 212.2 (s, CO), 212.1 (s, CO), 37.8 (d, $^{1}J_{C-P}$ = 17 Hz, C$_1$, Cy$_W$), 36.4 (d, $^{1}J_{C-P}$ = 23 Hz, C$_1$, Cy$_{Pt}$), 31.1 (d, $^{3}J_{C-P}$ = 2 Hz, C$_{3,5}$, Cy$_{Pt}$), 30.5 (s, C$_{3,5}$, Cy$_W$), 28.0 (m, 2 overlapping d, C$_{2,6}$, Cy$_{W+Pt}$), 26.8 (s, C$_4$, Cy$_W$), 26.7 (s, C$_4$, Cy$_{Pt}$), 4.2 (s, SiMe$_3$). ^{11}B{^{1}H} NMR (160 MHz, C_6D_6, 27 °C): δ 99 (br s). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6 , 27 °C): δ 76.8 (d, $^{4}J_{P-P}$ = 10 Hz, $^{1}J_{P-Pt}$ = 5001 Hz, P$_{Pt}$), 29.0 (d, $^{4}J_{P-P}$ = 10 Hz, $^{1}J_{P-W}$ = 243 Hz, $^{3}J_{P-Pt}$ = 106 Hz P$_W$). IR (toluene): 1982, 1882, 1835, 1786 cm^{-1}, ν (C═O). Anal. Calcd for $C_{46}H_{84}NBO_4P_2PtSi_2W$: C 45.17, H 6.92, N 1.15. Found: C 44.97, H 6.78, N 1.13.

Synthesis of [(Cy$_3$P)(OC)$_3$Cr(μ-CO){μ-BN(SiMe$_3$)$_2$}Pt(PCy$_3$)] (12). Solid **3** (0.045 g, 0.124 mmol) was added to a pale yellow solution of **9** (0.094 g, 0.124 mmol) in C_6D_6 (0.5 mL). The solution turned orange, and after 5 min orange crystals of **10** formed and were removed. The residual orange solution was layered with hexane and left in the glovebox for 4 days to let the solvent evaporate slowly. Orange crystals of **12** formed, which were recrystallized from toluene/hexane, yielding 0.020 g (15%). ^{1}H NMR (400 MHz, C_6D_6 , 23 °C): δ 2.30−1.20 (m, 66H, Cy), 0.63 (s, 18H, SiMe$_3$). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6 , 23 °C): δ 228.7 (dd, $^{2}J_{C-P}$ = 14 Hz, $^{4}J_{C-P}$ = 2 Hz, CO), 37.5 (d, $^{1}J_{C-P}$ = 14 Hz, C$_1$, Cy$_{Cr}$), 36.0 (d, $^{1}J_{C-P}$ = 23 Hz, C$_1$, Cy$_{Pt}$), 31.1 (d, $^{3}J_{C-P}$ = 2 Hz, C$_{3,5}$, Cy$_{Pt}$), 30.0 (s, C$_{3,5}$, Cy$_{Cr}$), 28.2 (d, $^{2}J_{C-P}$ = 10 Hz, C$_{2,6}$, Cy$_{Cr}$), 27.9 (d, $^{2}J_{C-P}$ = 11 Hz, C$_{2,6}$, Cy$_{Pt}$), 26.8 (s, C$_4$, Cy$_{Cr}$), 26.6 (d, C$_4$, $^{4}J_{C-P}$ = 1 Hz, Cy$_{Pt}$), 4.0 (s, SiMe$_3$). ^{11}B{^{1}H} NMR (160 MHz, C_6D_6, 27 °C): δ 97 (br s, $\omega_{1/2}$ = 2110 Hz). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6 , 23 °C): δ 70.1 (s, $^{1}J_{P-Pt}$ = 4972 Hz, P$_{Pt}$), 63.9 (s, $^{3}J_{P-Pt}$ = 127 Hz, P$_{Cr}$). IR (toluene): 1967, 1886, 1856, 1793 cm^{-1}, ν (C═O). Anal. Calcd for $C_{46}H_{84}NBCrO_4P_2PtSi_2$: C 50.63, H 7.75, N 1.28. Found: C 51.48, H 7.65, N 1.22.

Synthesis of [(Cy$_3$P)(OC)$_4$W{μ-BN(SiMe$_3$)$_2$}Pd(PCy$_3$)] (13). Solid **4** (0.030 g, 0.061 mmol) was added to a pale yellow solution of **8** (0.040 g, 0.061 mmol) in C_6D_6 (0.5 mL). The solvent was allowed to evaporate from the red reaction mixture in the glovebox. The solid residue was dissolved in 1.5 mL of hexane the next day and stored at −35 °C. After 3 days an orange solid of **13** was isolated (0.018 g, 26%). ^{1}H NMR (400 MHz, C_6D_6 , 21 °C): δ 2.17−1.60 (m, 66H, Cy), 0.63 (s, 18H, SiMe$_3$). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6 , 21 °C): δ 212.0 (dd, $^{2}J_{C-P}$ = 7 Hz, $^{4}J_{C-P}$ = 2 Hz, CO), 37.5 (d, $^{1}J_{C-P}$ = 17 Hz, C$_1$, Cy$_W$), 34.2 (d, $^{1}J_{C-P}$ = 11 Hz, C$_1$, Cy$_{Pd}$), 31.5 (d, $^{3}J_{C-P}$ = 5 Hz, C$_{3,5}$, Cy$_W$), 30.5 (s, C$_{3,5}$, Cy$_{Pd}$), 28.0 (d, $^{2}J_{C-P}$ = 11 Hz, C$_{2,6}$, Cy$_{Pd+W}$), 26.8 (s, C$_4$, Cy$_W$), 26.8 (s, C$_4$, Cy$_{Pd}$), 4.4 (s, SiMe$_3$). ^{11}B{^{1}H} NMR (96 MHz, C_6D_6, 23 °C): δ 98 (br s). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6 , 21 °C): δ 39.7 (d, $^{4}J_{P-P}$ = 11 Hz, P$_{Pd}$), 30.8 (d, $^{4}J_{P-P}$ = 11 Hz, $^{1}J_{P-W}$ = 367 Hz, P$_W$). IR (toluene): 1980, 1928, 1880, 1814 cm^{-1}, ν (C═O). Anal. Calcd for $C_{36}H_{84}NBO_4PdPSi_2W$: C 48.71, H 7.46, N 1.23. Found: C 49.31, H 7.21, N 1.10.

Synthesis of *trans*-[(Cy$_3$P)(OC)$_4$Cr═BN(SiMe$_3$)$_2$] (14). A yellow solution of **6** (0.090 g, 0.120 mmol) in C_6D_6 (1 mL) was photolyzed at 0 °C in a NMR quartz tube for 3 h. After that, the solvent of the dark brown reaction mixture was evaporated in vacuo. The solid residue was dissolved in 5 mL of hexane and stored at −80 °C. The first crystals were removed, because they were unreacted starting material. Then the solution was concentrated, and after 2 days at −80 °C crystals were isolated. They were recrystallized several times from hexane at −35 °C to remove colloidal palladium, yielding pale yellow crystals of **14** (0.021 g, 28%). ^{1}H NMR (400 MHz, C_6D_6 , 21 °C): δ 2.04−1.53 (m, 33H, Cy), 0.38 (s, 18H, SiMe$_3$). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6 , 21 °C): δ 224.3 (d, $^{2}J_{C-P}$ = 13 Hz, CO), 37.3 (d, $^{1}J_{C-P}$ = 13 Hz, C$_1$, Cy), 29.9 (s, C$_{3,5}$, Cy), 28.1 (d, $^{2}J_{C-P}$ = 10 Hz, C$_{2,6}$, Cy), 26.8 (s, C$_4$, Cy), 3.0 (s, SiMe$_3$). ^{11}B{^{1}H} NMR (96 MHz C_6D_6 , 23 °C): δ 94 (s, $\omega_{1/2}$ = 1100 Hz). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6 , 21 °C): δ 64.7 (s). IR (toluene): 1898, 1868 cm^{-1}, ν (C═O). Anal. Calcd for $C_{28}H_{51}NBCrO_4PSi_2$: C 54.62, H 8.35, N 2.28. Found: C 54.65, H 8.04, N 2.30.

Crystal Structure Determination. The crystal data of **6** and **14** were collected at a Bruker Apex diffractometer with CCD area detector and graphite-monochromated Mo Kα radiation, and the data of **11** were collected at a Bruker X8Apex diffractometer with CCD area detector and multilayer mirror monochromated Mo Kα radiation. The structures were solved using direct methods, refined with the Shelx software package (G. Sheldrick, University of Göttingen, 1997) and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to idealized positions and were included in structure factor calculations.

Crystal data for **6**: $C_{29}H_{51}BCrNO_5PPdSi_2$, M_r = 750.07, yellow block, 0.30 × 0.25 × 0.15, monoclinic space group $P2_1/n$, a = 10.293(4) Å, b = 16.264(7) Å, c = 21.535(9) Å, β = 90.285(8)°, V = 3605(3) Å^3, Z = 4, ρ_{calcd} = 1.382 g·cm^{-3}, μ = 0.946 cm^{-2}, $F(000)$ = 1560, T = 193(2) K, GOF = 1.040, R_1 = 0.0304, wR_2 = 0.0686, 8944 independent reflections [$2\theta \leq$ 56.56°] and 425 parameters.

Crystal data for **11**: $C_{46}H_{84}BNO_4P_2PtSi_2W$, M_r = 1223.01, orange block, 0.19 × 0.13 × 0.03, triclinic space group $P\bar{1}$, a = 12.1893(3) Å, b = 13.4380(4) Å, c = 16.1074(4) Å, α = 96.5790(10)°, β = 100.9850(10)°, γ = 96.4730(10)°, V = 2548.38(12) Å^3, Z = 2, ρ_{calcd} = 1.594 g·cm^{-3}, μ = 5.147 cm^{-2}, $F(000)$ = 1228, T = 100(2) K, GOF = 1.038, R_1 = 0.0247, wR_2 = 0.0584, 10 337 independent reflections [$2\theta \leq$ 52.76°] and 523 parameters.

Crystal data for **14**: $C_{28}H_{51}BCrNO_4PSi_2$, M_r = 615.66, yellow block, 0.25 × 0.16 × 0.10, monoclinic space group $P2_1/c$, a = 20.8563(14) Å, b = 9.1712(6) Å, c = 18.3901(12) Å, β = 100.7070(10)°, V = 3456.4(4) Å^3, Z = 4, ρ_{calcd} = 1.183 g·cm^{-3}, μ = 0.477 cm^{-2}, $F(000)$ = 1320, T = 193(2) K, GOF = 1.057, R_1 = 0.0417, wR_2 = 0.1074, 6830 independent reflections [$2\theta \leq$ 52.12°] and 343 parameters.

Crystallographic data for **6**, **11**, and **14** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-258168, CCDC-609382, and CCDC-609381, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Supporting Information Available: Crystal data in cif format. This material is available free of charge via the Internet at http://pubs.acs.org.

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