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Reactions with Electrophiles Control Isomerization from $\eta^5(\pi)$- to η^1(P)-Coordination of Phosphinyl-Substituted Benzophospholide Ligands

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The Ph_2P-functionalized phosphoniobenzo[*c*]phospholide **5** reacts with [Cr(CO)$_5$(cyclooctene)] and [Cr(CO)$_3$(naphthalene)] under site-selective n(P)-complexation at the Ph_2P moiety and π-complexation at the five-membered heterocycle, respectively, to give complexes **6** and **7**, which were characterized by spectroscopic data and an X-ray diffraction study of **6**. The attack of electrophiles E (E = alkyl$^+$, Ag$^+$, S, BH_3) on the π-complex **7** occurs at the pendant Ph_2P substituent to give unstable quaternization products that were in some cases detectable by NMR. The initial products decay either via decomplexation to metal-free quaternization products (for E = alkyl$^+$) or via a combination of decomplexation/isomerization reactions to give mixtures of free quaternization products and complexes **10a** and **13a** containing a Cr(CO)$_4$ unit that is chelated by a n(P)-coordinated benzophospholide moiety and an adjacent sulfur atom (for E = S) or a BH-σ-bond (for E = BH_3). These products as well as their tungsten analogues **10b** and **13b** were likewise accessible from the appropriate ligands and [M(CO)$_4$(norbornadiene)], and **10a**,**b** and **13b** were isolated from these reactions and characterized by spectroscopic and X-ray diffraction studies. The course of the studied reactions of **7** with electrophiles suggests that the destabilization of the primary quaternization products is controlled by increased weakening of the π-donor power of the ligand with increasing phosphonium character of the substituents at the benzophospholide moiety. The observed spontaneous $\pi(\eta^5)/\kappa^2$-*P*,σ-*BH*-coordination isomerization of a benzophospholide implies that the unusual coordination mode through a phosphorus lone pair and a BH-σ-bond is thermodynamically preferable to π-coordination through the five-membered ring.

Introduction

Heterocyclopentadienyls **I** are analogues of cyclopentadienyl (Cp) anions that are formally obtained when a CH moiety is replaced by an isoelectronic fragment E containing a different element of group 13−15 (E = BR$^-$, SiR, GeR, N, P, As, Sb).[1−3] Transition metal complexes of **I** mimic the well-known Cp complexes, but exhibit modulated metal reactivities due to the different electronic properties of the individual heterocyclic ligands, and in the context of the wide use of Cp complexes in catalysis and organometallic synthesis, the exploration of their chemistry is currently receiving considerable interest.[1−3] A substantial amount of work in this area has been dedicated to complexes of phospholides (**I**, E = P) whose electronic resemblance to Cp ligands is particularly close due to the very similar electronegativities of C and P, respectively.[2,3] Notwithstanding this similarity, phospholides are distinguished by their enhanced π-acceptor properties[3] and the presence of an additional lone pair at phosphorus, which may serve as a further metal-binding site.[4] Owing to these properties, metallocene analogue phospholyl complexes (phosphametallocenes) have been used as attractive ligands in catalytic processes involving soft transition metals.[4,5] During our investigations of the chemistry of benzannulated phospholide derivatives **II**−**IV**,[6] we have shown that the presence of positively charged phosphonio substituents renders the ligands weaker donors but enhances at the same time the π-acceptor power of the heteroaromatic ring.[7] The zwitterionic benzophospholide **1** displays therefore a balanced coordination behavior and may bind to transition metal atoms via both the phosphorus lone pair (n(P)-coordination, **2**) and the aromatic π-electron system, thus forming a stable half-sandwich complex **3** that is a structural analogue of an η^5-indenyl complex (Scheme 1).[7c] Cationic bisphosphoniobenzophospholides (**IV**) readily bind metal atoms via

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[1] ER = BR$^-$, SiR, GeR, N, P: (a) Review: A. P. Sadimenko, *Adv. Heterocycl. Chem.* **2001**, *79*, 115, and references therein.

[2] ER = N, P, As, Sb: Nief, F. *Eur. J. Inorg. Chem.* **2001**, 891.

[3] ER = P: Mathey, F. *Coord. Chem. Rev.* **1994**, *137*, 1. (b) Dillon, K. B.; Mathey, F.; Nixon, J. F. *Phosphorus: The Carbon Copy*; John Wiley: Chichester 1998, and references therein.

[4] Mathey, F. *J. Organomet. Chem.* **2002**, *646*, 15.

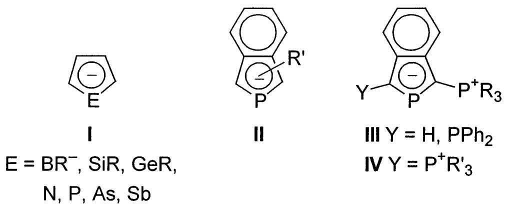
[5] Weber, L. *Angew. Chem., Int. Ed.* **2002**, *41*, 563.

[6] Gudat, D.; Bajorat, V.; Häp, S.; Nieger, M.; Schröder, G. *Eur. J. Inorg. Chem.* **1999**, 1169.

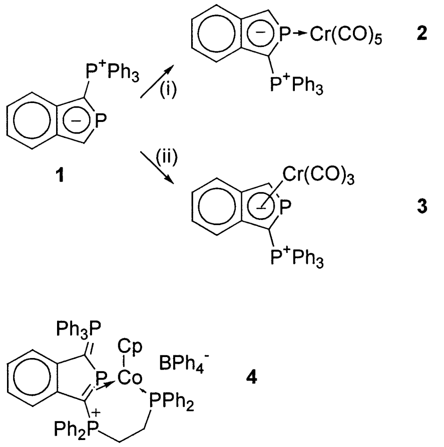
[7] (a) Gudat, D.; Schrott, M.; Nieger, M. *J. Chem. Soc., Chem. Commun.* **1995**, 1541. (b) Gudat, D.; Holderberg, A. W.; Korber, N.; Nieger, M.; Schrott, M.; *Z. Naturforsch.* **1999**, *54*, 1244. (c) Gudat, D.; Häp, S.; Szarvas, L.; Nieger, M. *Chem. Commun.* **2000**, 1637. (d) Gudat, D.; Häp, S.; Bajorat, V.; Nieger, M. *Z. Anorg. Allg. Chem.* **2001**, *627*, 1119. (e) Häp, S.; Nieger, M.; Gudat, D.; Betke-Hornfeck, M.; Schramm, D. *Organometallics* **2001**, *20*, 2679. (f) Gudat, D.; Häp, S.; Nieger, M. *J. Organomet. Chem.* **2002**, *643*, 181.

10.1021/om020404v CCC: $22.00

Chart 1



Scheme 1[a]



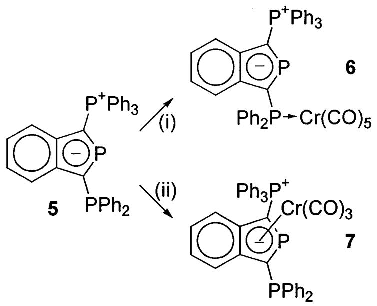
[a] (i) $[Cr(CO)_5(coe)]$, (ii) $[Cr(CO)_3(napht)]$.

the phosphorus lone pair,[7a,b,e] and their π-acceptor character is sufficient to allow the use of these ligands in hydroformylation catalysts.[7e] Despite a general preference of n(P)-coordination for these cations,[7] the recent isolation of the η^2-complex **4**[8] proves that formation of π-complexes is in principle feasible. At this point we became interested in establishing if cations of type **IV** may also form yet unknown η^5-complexes that could be potentially useful as novel π-acceptor ligands. Having synthesized the phosphinyl-substituted zwitterion **5**,[6] we reasoned that the target compounds might be accessible by conversion of **5** into a η^5-complex similar to the case of **3** and subsequent quaternization of the pendant Ph_2P moiety. We report here on the results of these experiments as well as the unexpected outcome of similar reactions of the formed π-complex with sulfur and $BH_3{\cdot}THF$.

Results and Discussion

Chemical Reactions and Spectroscopic Studies. The phosphinyl-substituted zwitterion **5** offers with the lone pairs of the two- and three-coordinate phosphorus atoms and the π-electrons of the fused ring system in principle three different metal-binding sites. To survey if, as in the case of **1**,[7c] site-selective complex formation is feasible, we reacted **5** with equimolar $[Cr(CO)_5(coe)]$ and $[Cr(CO)_3(napht)]$ (coe = cyclooctene, napht = naphthalene), respectively. Both reactions proceeded according to a ^{31}P NMR survey with quantitative formation of a single phosphorus-containing species. The products were isolated after precipitation with hexane and recrystallization from toluene, and their nature as complexes **6** and **7** (Scheme 2) was established by microanalytical and spectroscopic data (cf. Table 1) and for **6** by a single-crystal X-ray diffraction study. The selective coordination of the $Cr(CO)_5$ unit to the Ph_2P group in **6** is in accord with the easier steric accessibility and enhanced nucleophilicity[9] of this site. Comparison of the carbonyl regions in the IR spectra of **6** ($\bar{\nu}$ = 2058, 1932 cm^{-1}) and **2** ($\bar{\nu}$ = 2064, 1942, 1913 cm^{-1} [7c]) reveals slight red-shifts of the highest energy modes of the former, which is in accord with a lower π-acceptor capability of a Ph_2P as compared to a benzophospholide moiety. Key to the constitution assignment of π-complex **7** is the large negative coordination shift for the signal of the ring phosphorus atom ($\Delta\delta^{31}P = -175.5$), which is of similar magnitude to that in **3** ($\Delta\delta^{31}P = -157.8$); in contrast, the chemical shift of the PPh_2 moiety deviates little from that in **5** ($\Delta\delta^{31}P = +3$) and remains in the characteristic region of phosphines. Further worth mentioning is the chemical inequivalence of the two phenyl rings in the PPh_2 moiety, which is clearly visible in the ^{13}C NMR spectrum and owes to the planar chirality of the complex. The similarity of the carbonyl stretching modes of **7** ($\bar{\nu}$ = 1927, 1844, 1830 cm^{-1}) and **3** ($\bar{\nu}$ = 1925, 1835, 1826 cm^{-1} [7c]) further substantiates a close resemblance of the geometric and electronic structures of both complexes.

Scheme 2[a]



[a] (i) $[Cr(CO)_5(coe)]$, (ii) $[Cr(CO)_3(napht)]$.

Subsequent reaction of **7** with equimolar amounts of methyl iodide and benzyl bromide afforded cations **8a**,**b** besides minor amounts (<20%) of complex **6** (Scheme 3). The products were identified by comparison of their ^{31}P NMR data (Table 1) with those of authentic samples; the formation of further chromium-containing products can be inferred even though none was positively identified. Since monitoring the progress of the reaction by ^{31}P NMR disclosed no further observable intermediates, the formation of **8a**,**b** suggests that a hypothetical cationic π-complex formed by quaternization of the PPh_2 moiety of **7** is unstable and decays immediately with loss of the $Cr(CO)_3$ fragment; the generation of **6** as byproduct arises presumably from subsequent transfer of two CO ligands to unreacted starting material.

Attributing the instability of postulated η^5-complexes of **8a**,**b** to low π-nucleophilicity of a cationic ligand,[9,10] we reasoned that more stable complexes should be obtained if quaternization of the Ph_2P moiety in **7** was carried out with sulfur or $BH_3{\cdot}THF$ to give products with *neutral* thioxophosphorane or phosphine-borane ligands, respectively. In contrast to this anticipation, reaction of **7** with a stoichiometric amount of sulfur gave

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[8] Gudat, D.; Häp, S.; Nieger, M. *Z. Anorg. Allg. Chem.* **2001**, *627*, 2269.

[9] Häp, S.; Szarvas, L.; Nieger, M.; Gudat, D. *Eur. J. Inorg. Chem.* **2001**, 2763.

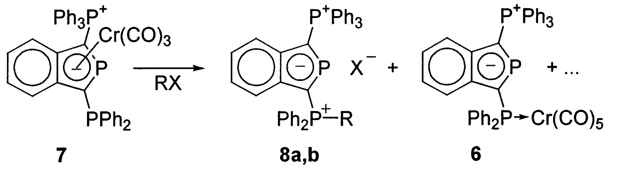
[10] Gudat, D. *Coord. Chem. Rev.* **1997**, *173*, 71, and references therein.

Table 1. ^{31}P NMR Data of Phosphoniobenzophospholide Derivatives 5−14 (at 30 °C, in THF) (E denotes a substituent at the exocyclic Ph_2P moiety, and M a η^5-coordinated metal fragment on the benzophospholide moiety)

	E	M	$\delta^{31}P$ ($-P^A-$)	$\delta^{31}P$ ($E-P^MPh_2$)	$\delta^{31}P$ ($-P^XPh_3$)	J_{AM} [Hz]	J_{AX} [Hz]	J_{MX} [Hz]
5[a]			218.4	−21.4	14.7	97.2	82.4	1.9
6	$Cr(CO)_5$		234.0	33.0	15.5	88.4	134.2	8.3
7		$Cr(CO)_3$	47.0	−17.7	21.3	7.9	61.0	5.1
8a	Me^+		234.7	16.4	12.3	92	92	8.3
8b	CH_2Ph^+		237.1	16.3	15.0	92.8	80.1	8.3
9[a]	S		228.3	35.0	16.1	88.4	88.7	8.1
10a	S-$Cr(CO)_4$		280.6					
10b	S-$W(CO)_4$		227.6[b]	27.4[c]	13.2	121.0	64.5	6.4
11[a]	BH_3		230.8	9.4	15.5	86.1	88.4	6.4
12	BH_3	$Cr(CO)_3$	54.0	11.1	22.0	35.6	64.9	
13a	BH_3-$Cr(CO)_4$		263.4					
13b	BH_3-$W(CO)_4$		217.2[d]	1.3	14.7	138.6	62.3	7.6
14	BH_3-$Cr(CO)_3$(THF)		279.0	−15.2	15.7	195.2	65.0	7.0

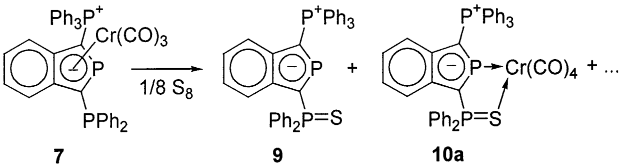
[a] Data from ref 9. [b] $^1J_{WPA}$ 242 Hz. [c] $^2J_{WPB}$ 9 Hz. [d] $^1J_{WPA}$ 264 Hz.

Scheme 3[a]



[a] **8a**: R = Me, X = I; **8b**: R = PhCH$_2$, X = Br.

Scheme 4



likewise no evidence for a stable η^5-complex, but afforded a mixture of thioxophosphorane **9** and chromium complex **10a** as the only phosphorus-containing products (Scheme 4). While **9** was identified by comparison of its ^{31}P NMR data with an authentic sample, the identity of complex **10a** was confirmed by its independent synthesis from **9** and [$Cr(CO)_4$(nbd)] (nbd = norbornadiene); a similar reaction with [$W(CO)_4$(nbd)] afforded also the tungsten complex **10b**. The chelating κ^2-*P*,*S*-coordination of the benzophospholide ligands in **10a**,**b** was deduced from NMR data (Table 1) and confirmed by X-ray diffraction studies. Key spectroscopic features that substantiate a shift from π- to n(P)-coordination include the substantial deshielding of the ring phosphorus atoms ($\Delta\delta^{31}P = +233.6$ (**10a**), +180.6 (**10b**) vs **7**), and for **10b** the presence of ^{183}W satellites with couplings of $^1J_{WP} = 242$ Hz for the endocyclic and $^2J_{WP} = 9$ Hz for the P=S phosphorus atom.

Reaction of π-complex **7** with $BH_3{\cdot}THF$ afforded according to a ^{31}P NMR survey a mixture of three phosphorus-containing products. Each species gave rise to an AMX-type pattern whose most shielded signal consisted of a broad line without resolved fine structure. Such line broadening is a typical consequence of spin coupling to an adjacent quadrupolar boron nucleus, and we thus assign all products as Lewis-acid/base adducts formed by attachment of BH_3 to the Ph_2P moiety. One product was readily identified as known zwitterion **11**[9] by comparison of its ^{31}P NMR data with an authentic sample, and the remaining ones were appointed as novel complexes **12** and **13a** (Scheme 5). Prolonged reaction times lead to complete conversion of **12** into **11** and **13a**.

The assignment of **12** as a π-complex was in the first place deduced from the similar ^{31}P NMR shift of the endocyclic phosphorus atom as compared to **7** (cf. Table 1) and was further confirmed by independent synthesis of a mixture of **12** and **13a** by reaction of zwitterion **11** with excess [$Cr(CO)_3$(napht)]. Assignment of the constitution of **13a** as a complex with a n(P)-coordinated benzophospholide was suggested by the substantial deshielding of the ring phosphorus atom ($\Delta\delta^{31}P = +216.4$ vs **7**) and further corroborated by the observation that this complex was also formed in approximately 25% yield (from integration ^{31}P NMR spectra) by reaction of equimolar amounts of [$Cr(CO)_4$(nbd)] and the borane adduct **11** (no **12** was detectable under these conditions); the low yield of complex contrasts with the smooth formation of **10a** from **9** and the chromium complex, but is in accord with the reputedly low stabilities of other known borane−transition metal complexes.[11] Addition of [$Cr(CO)_4$(nbd)] in large excess increased the yield of **13a**, but favored also formation of **6** as byproduct and rendered separation of the mixture and isolation of **13a** unfeasible. A higher selectivity was observed in the reaction of **11** and [$W(CO)_4$(nbd)]. Extensive formation of the tungsten complex **13b** occurred with only 2 equiv of the olefin complex, and the product was readily isolated and characterized by spectroscopic and X-ray diffraction studies.

The ^{31}P NMR spectrum of **13b** displays an AMX pattern similar to that of **13a**. The resonances of the P atoms in the ring and the phosphine-borane moiety exhibit small negative coordination shifts ($\Delta\delta^{31}P = -14.5$ (−P−), −10.8 (P−B) vs **11**), and n(P)-coordination of the ring phosphorus atom is clearly evidenced by a characteristic set of ^{183}W satellites ($^1J_{WP} = 264$ Hz). The ^{1}H NMR spectrum displays a single broad signal ($\delta^1H = -1.33$) attributable to the BH_3 group, which is likewise more shielded than that in **11** ($\delta^1H = 1.41$) and changes under ^{11}B decoupling into a sharp multiplet. Application of additional selective ^{31}P decoupling al-

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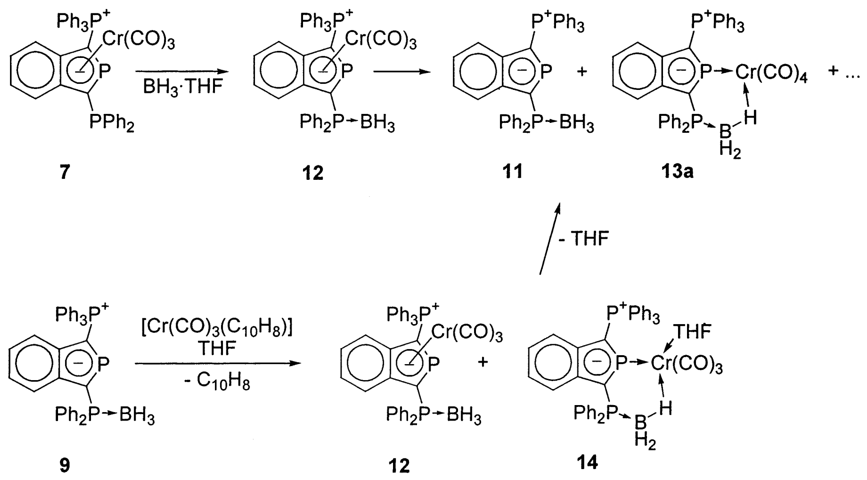
[11] (a) McNamara, W. F.; Duesler, E. N.; Paine, R. T.; Ortiz, J. V.; Kölle, P.; Nöth, H. *Organometallics* **1986**, *5*, 380. (b) Shimoi, M.; Nagai, S.; Ichikawa, M.; Kawano, Y.; Katoh, K.; Uruichi, M.; Ogino, H. *J. Am. Chem. Soc.* **1999**, *121*, 11704. (c) Kakizawa, T.; Kawano, Y.; Shimoi, M. *Organometallics* **2001**, *20*, 3211.

Scheme 5



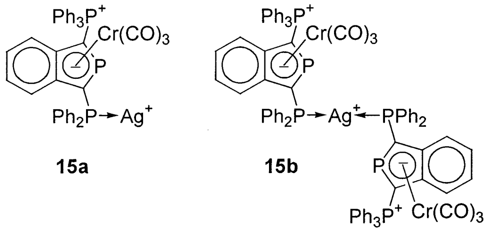
lowed the assignment of the $^2J_{P-B-H}$ (9.0 Hz) and $^2J_{P-W-H}$ (5.1 Hz) couplings. The increase of the latter compared to $^4J_{P-C-P-B-H} = 2.5$ in **12** and the observation of ^{183}W satellites with $^1J_{WH} = 14$ Hz clearly confirm the attachment of the BH_3 unit to the metal. In view of the X-ray data (see below) which disclose the presence of one coordinated and two terminal BH bonds in the crystal, the chemical equivalence of the BH_3 hydrogens in solution ^{1}H NMR spectra (low-temperature spectra gave no evidence for a decoalescence down to −80 °C) suggests a fluxional molecular structure in which rotation of the BH_3 moiety induces rapid scrambling of coordinated and terminal BH bonds. Similar dynamic effects have been previously observed for other transition metal complexes of σ-BH-coordinated borane/Lewis-base adducts.[11]

Further ^{31}P NMR studies revealed that the formation of chromium complex **13a** in the reaction of **11** with [Cr(CO)$_3$(napht)] was preceded besides **12** by that of a further transient borane complex which gave rise to an AMX pattern with chemical shifts similar to **13a** (Table 1). Regarding that this intermediate was observable only when the reaction was conducted in THF, its molecular structure is tentatively assigned as chelate complex **14** (Scheme 5).

The spectroscopic evidence for the formation of a π-complex **12** prompted us to investigate if the Ph_2P moiety of **7** might as well be able to bind to a second transition metal rather than a main group electrophile, thus giving rise to novel binuclear complexes with a n(P),π-bridging phosphinylbenzophospholide. To this end, we reacted **7** with the complexes [M(CO)$_5$(coe)] (M = Cr, W), which are suitable reagents for the transfer of 16e-metal fragments, and with silver triflate. The reactions with the two olefin complexes afforded according to ^{31}P NMR studies mixtures of several products. The main product was in both cases identified as chromium complex **6**, whose formation from **7** and [W(CO)$_5$(coe)] suggested that a reaction involving intermolecular CO scrambling rather than the expected transfer of an intact M(CO)$_5$ fragment had occurred. In view of the these unexpected mechanistic complications, reactions of **7** with metal carbonyls were not pursued further.

A ^{31}P NMR study of the reaction of **7** with 1 equiv of silver triflate gave evidence for the formation of rather unstable heterobimetallic complexes which decomposed during prolonged storage or attempts toward workup of the reaction mixture. Partial constitutional assignment was feasible from low-temperature ^{31}P and ^{109}Ag NMR data. The ^{31}P NMR spectra show three groups of signals centered around 49, 21, and 1.5 ppm attributable to the phosphorus atoms of benzophospholide, triphenylphosphonio, and diphenylphosphinyl moieties. The chemical shift of the ring phosphorus atom suggests that the π-coordinated Cr(CO)$_3$ moiety is still present, and a characteristic splitting by spin coupling to $^{107/109}$Ag nuclei on the signal attributable to the phosphorus in the Ph_2P moiety indicates coordination of Ag^+ at this site (a 2D ^{31}P,^{109}Ag HMQC spectrum yielded $^1J_{109Ag,P} = 590$ Hz and δ^{109}Ag = 668). The observed data are compatible with the presence of a 1:1 (**15a**, Chart 2) or a 2:1 (**15b**) complex, or a mixture of both, but the poor resolution precluded a more comprehensive spectral analysis, and a concise structural assignment was unfeasible. The appearance of new signals between 230 and 250 ppm in the course of the decomposition process suggested that the initially formed complexes decay via loss of the π-coordinated Cr(CO)$_3$ fragment.

Chart 2



Crystal Structure Studies. Crystals of **6**·CH_2Cl_2, **10a**·THF, **10b**, and **13b**·0.5toluene suitable for single-crystal X-ray structure determinations were obtained by crystallization from CH_2Cl_2/THF and toluene/THF, respectively. Representations of the molecular structures of **6**, **10a**, and **13b** are given in Figures 1−3 together with important bond distances and angles. The molecular structure of **10b** differs only insignificantly from that of **10a** and is not shown.

The bonding parameters in the P-coordinated phosphoniobenzophospholide moiety in complex **6** differ, apart from minor shortenings of the exocyclic P(2)−C(2) (1.786(2) Å) and the endocyclic P(1)−C(9) (1.748(2) Å)

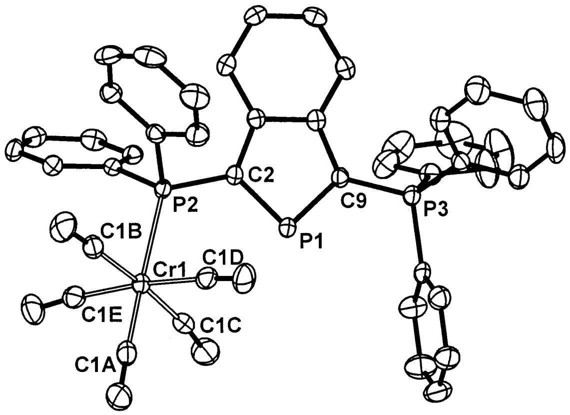


Figure 1. ORTEP representation of the molecular structure of **6**. Thermal ellipsoids are drawn at the 50% probability level, and H atoms have been omitted for clarity. Selected bond lengths (Å): Cr(1)−C(1A) 1.840(3), Cr(1)−C(1D) 1.892(3), Cr(1)−C(1E), 1.893(3), Cr(1)−C(1B) 1.899(3), Cr(1)−C(1C) 1.906(3), Cr(1)−P(2) 2.4170(7), P(1)−C(2) 1.734(2), P(1)−C(9) 1.748(2), C(2)−C(3) 1.446(3), C(2)−P(2) 1.786(2), C(3)−C(4), 1.417(3), C(3)−C(8), 1.421(3), C(4)−C(5) 1.375(3), C(5)−C(6) 1.401(3), C(6)−C(7) 1.374(3), C(7)−C(8) 1.418(3), C(8)−C(9) 1.443(3), C(9)−P(3) 1.732(2).

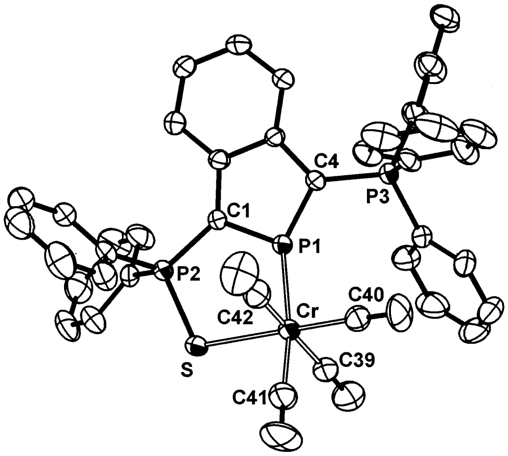


Figure 2. ORTEP representation of the molecular structure of **10a**. Thermal ellipsoids are drawn at the 50% probability level, and H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Cr−C(39) 1.899(5), Cr−C(40) 1.821(4), Cr−C(41) 1.844(4), Cr−C(42) 1.882(5), Cr−P(1) 2.3262(10), Cr−S 2.5056(10), P(1)−C(1) 1.714(3), P(1)−C(4) 1.729(3), C(1)−P(2) 1.758(3), C(4)−P(3) 1.751(3), P(2)−S 2.0184(12), P(1)−Cr−S 81.36(3), P(2)−S−Cr 108.45(4).

bonds, not significantly from the corresponding values in the free ligand **5** (P(2)−C(2) 1.8092(13), P(1)−C(9) 1.7623(13) Å[9]). The distorted octahedral coordination geometry at the chromium atom with a Cr(1)−P(2) distance of 2.4170(7) Å and the relative shortening of the Cr(1)−C(1A) bond (1.840(3) Å) to the *trans*-CO with respect to those to the *cis*-CO ligands (1.892(3)−1.906(3) Å) are typical features of phosphine-$Cr(CO)_5$ complexes and require no further comments.

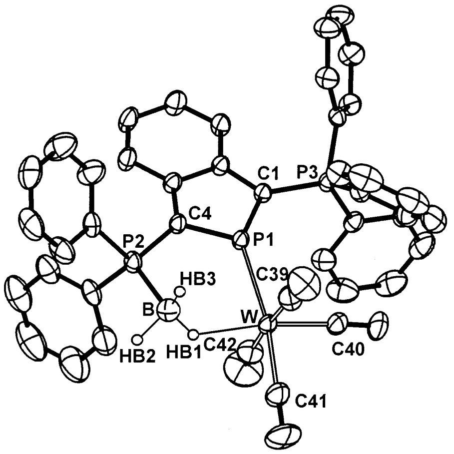


Figure 3. ORTEP representation of the molecular structure of **13b**. Thermal ellipsoids are drawn at the 50% probability level, and H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): W−C(39) 2.049(4), W−C(40) 1.958(3), W−C(41) 1.972(3), W−C(42) 2.019(4), W−HB1 2.02, (3)W−P(1) 2.4684(7), P(1)−C(4) 1.722(3), P(1)−C(1) 1.738(3), P(2)−C(4) 1.772(3), P(3)−C(1) 1.744(2), P(2)−B 1.943(4), B−HB1 1.15(3), B−HB2 1.15(5), B−HB3 0.90(3), HB1−W−P(2) 84, B−HB1−W 126.

The n(P)-coordination of the benzophospholide moiety in the chromium complex **10a** induces a shortening of the P(1)−C(1) (1.714(3) Å) and P(1)−C(4) (1.729(3) Å) bonds and a widening of the C(1)−P(1)−C(4) angle (94.3(2)°) as compared to the free ligand **9** (1.7353(19)/1.7540(19) Å/91.50(9)° [9]). These effects as well as the slightly pyramidal coordination environment of the coordinated P(1) atom (sum of bond angles 356.0(4)°) have precedence in other complexes with terminal benzophospholide ligands.[7] The lengthening of the P(2)−S bond upon coordination (2.0184(12) vs 1.9690(7) Å in **9**[7]) and the Cr−S distance (2.5056(10) Å) represent typical values for thioxophosphorane metal complexes (P=S: free 1.945 ± 0.035, coordinated 1.998 ± 0.027,[12] Cr−S 2.500 in $Cr(CO)_5(Me_3PS)$[13]). The five-membered chelate ring adopts a flat twist conformation. The small bite angle of the bidentate ligand (P(1)−Cr−S 81.36(3)°) induces a marked distortion of the octahedral coordination geometry at the chromium atom. Further planarization of the chelate ring might reduce this distortion, but is presumably prevented by steric interference between the ancillary CO ligands and the bulky Ph_3P group. The Cr−C(41) distance (1.844(4) Å) opposite the Cr−P(1) bond and the Cr−C(39) (1.899(5) Å) and Cr−C(42) bonds (1.882(5) Å) in the *trans*-$Cr(CO)_2$ unit are similar to the distances of *cis*- and *trans*-CO ligands in **6**, while the Cr−C(40) bond (1.821(4) Å) is still shorter. The trend in Cr−C distances points to increasing π-acceptor power of the *trans*-ligands in the order thioxophosphorane < benzophospholide < CO. The structural parameters of the tungsten complex **10b** display—apart from a further slight reduction of the chelate bite angle (P−W−S angle 79.88(6)°), which is attributable to the larger radius of a tungsten as compared to a chromium atom—no significant deviations from those of **10a**.

The intraligand distances and angles in the phosphinylbenzophospholide moiety of complex **13b** are essentially identical to those in **10a**,**b**, and the P(2)−B distance (1.943(4) Å) is indistinguishable within experimental error from that in the free ligand **11** (1.9315(19) Å[9]). The P(1) atom adopts a pyramidal coordination

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(12) Results of a quest in the CCSD database for phosphine sulfides $X_3P=S$ and their transition metal complexes.

(13) Baker, E. N.; Reay, B. R. *J. Chem. Soc., Dalton Trans.* **1973**, 2205.

geometry (sum of bond angles 355.3(3)°) similar to that in **10a**,**b**. The positions of the BH hydrogen atoms were located and refined isotropically, and the borane moiety is despite some irregularities in B−H distances and P−B−H angles best described as containing two terminal and one bridging B−H bond that is σ-coordinated to the tungsten atom. The B−H(B1)−W angle of 126° is close to those in complexes $[M(CO)_5(\eta^1\text{-}H_3BPMe_3)]$ (M = Cr, 130(8)°; M = W, 128(7)° [11b]) and $[CpMn(CO)_2(\eta^1\text{-}H_3BEMe_3)]$ (E = N, 142(3)°; E = P, 129(3)° [11c]), and the W···B distance (2.847(4) Å) is comparable to that in $[W(CO)_5(\eta^1\text{-}H_3BPR_3)]$ (R = Me, Ph, 2.81−2.86 Å[11b]). Together, these features suggest descriptions of the mode of coordination for the borane as end-on and of the metal−ligand intraction as an "open" three-center two-electron bond.[11b,c] Using this notation, the tungsten atom in **13b** is coordinated in a distorted octahedral geometry defined by the four carbonyls and the P(1) and the H(B1) atoms of a κ^2-*P*,σ-*BH*-chelating ligand **11**. The conformation of the formed six-membered chelate ring is intermediate between twist- and chair-conformations, and the chelate bite angle (H(B1)−W−P(2) 84°) is similar to **10a**,**b**. The trend in W−C distances parallels that found for **10a**,**b**, and bond distances increase depending if the carbonyl is in *trans*-position to the hydride (W−C(40) 1.958(3) Å), benzophospholide (W−C(41) 1.972(3) Å), or a second carbonyl ligand (W−C(39) 2.049(4), W−C(42) 2.019(4) Å).

A Comment on Reaction Pathways. The outcome of the reactions of the η^5-benzophospholide complex **7** with different electrophiles E can be rationalized in terms of a common pathway via initial quaternization of the exocyclic Ph_2P moiety by the electrophile to afford a π-complex of a (pseudo)bisphosphonio-substituted benzophospholide, which then undergoes subsequent decomposition. The fact that the primary π-complex is observable by ^{31}P NMR for E = Ag^+, BH_3, but not for E = S, R^+, suggests that larger positive charge densities (i.e., higher phosphonium character) at the phosphorus atom of the Ph_2PE moiety[9] have a destabilizing influence, which is easily rationalized in terms of lower π-nucleophilicity of the benzophospholide ligand.

The decay of the primary complex occurs in the case of E = R^+ quantitatively via formation of a bisphosphoniobenzophospholide cation and loss of the $Cr(CO)_3$ fragment. In the case of E = S, BH_3, which have both electrophilic and nucleophilic properties, the initial π-complex decays to give a mixture of the free ligand and a chelate complex in which the lone pair of the ring phosphorus atom and either a sulfur lone pair or a BH-σ-bond occupies two adjacent coordination sites of a $Cr(CO)_4$ moiety. Two likely mechanisms may be envisaged for the formation of this mixture. The first one involves dissociation of the initial complex to give transient $[Cr(CO)_3(THF)_3]$, subsequent ligand scrambling to yield $[Cr(CO)_4(THF)_2]$ besides further unidentified chromium-containing products, and final recombination of the benzophospholide and the $Cr(CO)_4$ fragment to a chelate complex. Alternatively, it can be conceived that the initial π-complex reacts under take-up of a solvent molecule (THF) and π/n(P)-coordination isomerization to a complex in which the ring phosphorus atom and a sulfur or BH moiety chelates a $Cr(CO)_3(THF)$ moiety; this intermediate then decays in part via cleavage of the metal fragment to the free phosphorus-containing ligand and in part via displacement of the coordinated solvent by another CO (from the liberated $Cr(CO)_3$ moiety) to a tetracarbonyl complex. Even if the observation of an intermediate of presumed constitution **14** (cf. Scheme 5) in the reaction of **11** with $[Cr(CO)_3(napht)]$ appears as an argument in favor of an associative reaction, a dissociative mechanism or a competition between both pathways may currently not be completely ruled out.

An interesting aspect of the π/n(P)-coordination isomerization is that, apart from any mechanistic details, the observed reactivities indicate that η^5-coordination of a benzophospholide moiety with two (quasi)-phosphonio substituents ($-P^{(+)}R_3$, $-R_2P^{(+)}\text{-}S^{(-)}$, $-R_2P^{(+)}\text{-}BH_3^{(-)}$) is energetically less favorable than a terminal κ^2-*P*,*S*- or κ^2-*P*,σ-*BH*-coordination, respectively. Even though the capability of phosphine sulfides to form strong dative bonds to a transition metal is well established, σ-donating boranates or borane/Lewis-base complexes are normally considered as much weaker ligands,[11] and the observed trend to trade $\pi(\eta^5)$- for σ-BH-coordination may therefore be considered as remarkable and points to an unusually weak π-donating power of the zwitterionic or cationic benzophospholides.

Experimental Section

General Comments. All manipulations were carried out under dry argon. Solvents were dried by standard procedures. NMR spectra: Bruker AMX300 (^1H 300.1 MHz, ^{31}P 121.5 MHz, ^{13}C 75.4 MHz, ^{11}B 96.3 MHz, ^{109}Ag 14.0 MHz) in THF-d_8 at 30 °C if not stated otherwise; 2D $^{31}P\{^1H\},^{109}Ag$ HMQC spectra were recorded using published pulse sequences;[14] chemical shifts referenced to external TMS (^1H,^{13}C), 85% H_3PO_4 (Ξ = 40.480747 MHz, ^{31}P), aqueous Ag^+ (Ξ = 4.653623 MHz, ^{109}Ag); $BF_3\cdot OEt_2$ (Ξ = 32.083971 MHz, ^{11}B); positive signs of chemical shifts denote shifts to lower frequencies, coupling constants are given as absolute values. Prefixes *i*-, *o*-, *m*-, and *p*- denote atoms of phenyl substituents, and atoms in the benzophospholide ring are denoted as 4-C, 5-H, etc.; assignment of resonances was derived in ambiguous cases from ^1H,^{13}C and ^1H,^{31}P HMQC NMR spectra. MS: Kratos Concept 1H, Xe-FAB, m-NBA matrix. Elemental analyses: Heraeus CHNO-Rapid. The amount of cocrystallized solvents was verified by integration of suitable ^1H NMR signals. Melting points were determined in sealed capillaries. ^{31}P NMR data are listed in Table 1.

[Pentacarbonyl-{3-diphenylphosphinyl-1-triphenylphosphoniobenzo[*c*]phospholide-κ^1-*P*}chromium(0)] (6). $[Cr(CO)_5(coe)]$ (100 mg, 0.33 mmol) and **5** (200 mg, 0.33 mmol) were dissolved in 10 mL of THF and stirred for 6 h at room temperature. The red solution was then concentrated in vacuo to a final volume of 4 mL, and 15 mL of hexane was added. The precipitated orange solid was collected by filtration, washed with a little hexane, and dried in high vacuum to give 160 mg (0.21 mmol, 69%) of **6**, mp 214 °C. Anal. Calcd for $C_{43}H_{29}CrO_5P_3$ (770.6)·hexane: C 68.69; H 5.06. Found: C 69.49; H 5.2. ^1H NMR: δ 6.4−6.6 (4H) [4-H to 7-H]; 7.06−8.12 (25H) [C_6H_5]. $^{13}C\{^1H\}$ NMR: δ 97.4 (ddd, $^1J(P^AC)$ = 57.2 Hz, $^1J(P^XC)$ = 99.4 Hz, $^3J(P^MC)$ = 15.5 Hz; C-1), 118.8 (s; C-5), 119.7 (d, $^4J(P^XC)$ = 1.0 Hz; C-6), 120.7 (d, $^3J(P^AC)$ = 3.4 Hz; C-4), 122.8 (dd, $^3J(P^AC)$ = 4.5 Hz, $^3J(P^XC)$ = 4.5 Hz; C-7), 125.1 (dd, $^1J(P^XC)$ = 89.7 Hz, $^3J(P^AC)$ = 2.3 Hz; *i*-C(PPh$_3$)), 129.6 (d, $^3J(P^XC)$ = 12.4 Hz; m−C(PPh$_3$)), 128.1 (d, $^3J(P^MC)$ = 9.2 Hz;

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[14] Gudat, D. In *Annual Reports in NMR Spectroscopy*; Webb, G. A., Ed.; Academic Press: San Diego, 1999; Vol. 38, p 139, and references therein.

m-C(PPh$_2$)), 129.0 (d, ^4J(P^{M}C) = 2.1 Hz; p−C(PPh$_2$)), 132.4 (dd, ^2J(P^{M}C) = 10.8 Hz, ^4J(P^{A}C) = 1.1 Hz; o-C(PPh$_2$)), 133.6 (d, ^4J(P^{X}C) = 2.9 Hz; p-C(PPh$_3$)), 134.5 (dd, ^2J(P^{X}C) = 10.3 Hz, ^4J(P^{A}C) = 1.5 Hz; o-C(PPh$_3$)), 137.0 (ddd, ^1J(P^{A}C) = 51.1 Hz, ^1J(P^{M}C) = 34.4 Hz, ^3J(P^{X}C) = 13.5 Hz; C-3), 138.4 (dd, ^1J(P^{M}C) = 35.0 Hz, ^3J(P^{A}C) = 5.6 Hz; *i*-C(PPh$_2$)), 144.0 (dd, ^2J(P^{A}C) = 4.7 Hz, ^2J(P^{M}C) = 16.5 Hz; C-3a), 145.2 (dd, ^2J(P^{A}C) = 9.3 Hz, ^2J(P^{X}C) = 9.3 Hz; C-7a), 218.0 (dd, ^2J(P^{M}C) = 13.5 Hz, ^4J(P^{A}C) = 4.1 Hz; *cis*-CO), 232.2 (d, ^2J(P^{M}C) = 7.6 Hz; *trans*-CO). MS ((+)-Xe-FAB, mNBA): *m*/*e* (%) 714 (80) [M$^+$ − 2 CO]; 630 (100) [M$^+$ − 5 CO]. IR (CH$_2$Cl$_2$, CaF$_2$): $\bar{\nu}$ = 2058, 1932 cm^{-1} (νCO).

[Tricarbonyl-η^5-{3-diphenylphosphinyl-1-triphenylphosphoniobenzo[*c*]phospholide} chromium(0)] (7). A mixture of **5** (210 mg, 0.35 mmol) and [Cr(CO)$_3$(napht)] (100 mg, 0.35 mmol) was dissolved in 10 mL of THF and stirred for 12 h at room temperature. The red solution was then evaporated in vacuo, and residual naphthalene sublimed off at 40 °C in high vacuum. The residue was dissolved in 5 mL of toluene and layered with 15 mL of pentane. A red precipitate formed, which was filtered off and dried in high vacuum to give 170 mg (0.24 mmol, 69%) of **6**, mp 217 °C. Anal. Calcd for $C_{41}H_{29}CrO_3P_3$ (714.6)·pentane: C 70.23; H 5.25. Found: C 70.76; H 4.77. ^{1}H NMR: δ 6.73−7.05 (m, 2H), 7.23 (m, 1H), 8.49 (m, 1H) [4-H to 7-H]; 7.07−8.30 (25H) [C$_6$H$_5$]. ^{13}C{^{1}H} NMR: δ 118.7 (ddd, ^1J(P^{A}C) = 6.7 Hz, ^1J(P^{M}C) = 4.1 Hz, ^3J(P^{X}C) = 2.7 Hz; C-3); 118.8 (dd, ^1J(P^{A}C) = 4.5 Hz, ^1J(P^{X}C) = 8.7 Hz; C-1); 121.2 (d, J(P^{a}C) = 0.8 Hz), 122.7 (s), 122.7 (s), 123.0 (s), [C-4 to C-7]; 123.2 (dd, ^1J(P^{X}C) = 90.0 Hz, ^3J(P^{A}C) = 1.3 Hz, *i*-C(PPh$_3$)), 125.2 (m), 127.4 (m) [C-3a/7a)]; 128.0 (s), 125.9 (s) [p−C(PPh$_2$)]; 128.5 (d, ^3J(P^{M}C) = 11.1 Hz), 127.7 (d, ^3J(P^{M}C) = 7.1 Hz [m-C(PPh$_2$)]; 129.7 (d, ^3J(P^{X}C) = 12.4 Hz; m−C(PPh$_3$)), 134.3 (d, ^{4}J(P^{X}C) = 2.7 Hz; p-C(PPh$_3$)), 134.5 (dd, ^2J(P^{M}C) = 16.5 Hz, ^4J(P^{A}C) = 1.8 Hz), 133.1 (dd, ^2J(P^{M}C) = 19.4 Hz, ^4J(P^{A}C) = 1.0 Hz [o-C(PPh$_2$)]; 134.7 (dd, ^2J(P^{X}C) = 9.9 Hz, ^2J(P^{A}C) = 1.7 Hz; o-C(PPh$_3$)), 140.3 (d, ^1J(P^{M}C) = 15.5 Hz, ^1J(P^{A}C) = 1.5 Hz), 137.3 (d, ^1J(P^{M}C) = 8.9 Hz, ^1J(P^{A}C) = 8.9 Hz) [*i*-C(PPh$_2$)]; 236.1 (d, J(P^{A}C) = 2.9 Hz; CO). MS ((+)-Xe-FAB, mNBA): *m*/*e* (%) 714 (15) [M$^+$], 646 (50) [M$^+$ − C$_3$O$_2$], 630 (100) [M$^+$ − 3 CO]. IR (CH$_2$Cl$_2$, CaF$_2$): $\bar{\nu}$ = 1927, 1844, 1830 cm^{-1} (νCO).

Reaction of 7 with Electrophiles (General Procedure). **7** (250 mg, 0.35 mmol) was dissolved in 10 mL of THF, and an equimolar amount of the appropriate electrophile added either as pure solid (S$_8$, AgOTf) or as solution in THF (MeI, PhCH$_2$-Br, BH$_3$). After dissolution of all reactants, a portion of the reaction mixture was transferred to an NMR tube and the reaction monitored by ^{31}P NMR spectroscopy.

1-Methyldiphenylphosphonio-3-triphenylphosphoniobenzo[*c*]phospholide (8a). MeI (approximately 100 mg, 0.7 mmol) was added via syringe to a stirred solution of **5** (200 mg, 0.35 mmol) in 5 mL of toluene. The solution was gently warmed, and stirring was continued until a cream precipitate separated. The product was collected by filtration, washed with hexane and ether, and dried in a vacuum to yield 229 mg (32 mmol, 92%) of **8a** (mp > 250 °C) as an off-white powder, which was characterized by its ^{1}H and ^{31}P NMR data. ^{1}H NMR (CD$_2$-Cl$_2$): δ 2.73 (dd, ^2J(P^{M}H = 12.9 Hz, ^4J(P^{A}H) = 1.8 Hz, 3H, CH$_3$); 6.90−7.05 (m, 2H) [5-H/6-H]; 7.05 (m, 1H), 7.17 (m, 1H) [4-H/7-H]; 7.60−7.86 (25H) [C$_6$H$_5$].

1-Benzyldiphenylphosphonio-3-triphenylphosphoniobenzo[*c*]phospholide (8b). Reaction of **5** and PhCH$_2$Br was conducted as described above, yielding 750 mg (0.31 mmol, 90%) of **8b**, mp 172 °C (dec). ^{1}H NMR (CDCl$_3$): δ 4.57 (d, ^2J(P^{M}H = 14.0 Hz, 2H, CH$_2$); 6.70−7.30 (9H; 4-H to 7-H, C6H5-(benzyl); 7.30−7.80 (25H) [C$_6$H$_5$]. MS ((+)-Xe-FAB, mNBA): *m*/*e* (%) 669 (100) [M$^+$ − Br].

[Tetracarbonyl-{1-triphenylphosphonio-3-diphenylthioxophosphoranylbenzo[*c*]phospholide-κ^2-*P*,*S*}chromium(0)] (10a). [Cr(CO)$_4$(nbd)] (135 mg, 0.53 mmol) and **9** (220 mg, 0.35 mmol) were dissolved in 10 mL of THF. The resulting solution was stirred for 24 h at room temperature and layered with 10 mL of hexane. The formed dark red precipitate was collected by filtration and dried in a vacuum to give 223 mg (0.29 mmol, 80%) of **10a**, mp 157 °C (dec). Anal. Calcd for $C_{42}H_{29}CrO_4P_3S$ (774.7): C 65.12; H 3.77; S 4.14. Found: C 63.7; H 4.3; S 4.4. ^{1}H NMR: δ 6.51−6.61 (m, 2H; 5-H/6-H), 6.72 (m, 1H; 3-H), 7.06 (m, 1H, 7-H); 7.45 (m, 4H; m-H(PPh$_2$); 7.52 (m, 2H; p-H(PPh$_2$); 7.64 (m, 6H; m-H(PPh$_3$); 7.74 (m, 3H; p-H(PPh$_3$); 7.83 (m, 4H; o-H(PPh$_2$); 8.01 (m, 6H; o-H(PPh$_3$). ^{13}C-{^{1}H} NMR: δ 98.4 (dd, ^1J(P^{X}C) = 173 Hz, ^1J(P^{A}C) = 30 Hz; C-1)); 118.9 (d, J(PC) = 8.4 Hz; C-6)); 119.2 (dd, J(PC) = 4.2, 4.3 Hz; C-5)); 119.6 (s; C-4/7); 120.4 (d, J(PC) = 1.3 Hz; C-4/7); 125.0 (dd, ^1J(P^{X}C) = 90.4 Hz, ^3J(P^{A}C) = 2.1 Hz; *i*-C(PPh$_3$)); 129.2 (d, ^3J(P^{M}C) = 12.6 Hz; m-C(PPh$_2$)); 130.3 (d, ^3J(P^{X}C) = 12.6 Hz; m-C(PPh$_3$)); 132.3 (d, ^2J(P^{M}C) = 2.9 Hz; p-C(PPh$_2$)); 133.2 (d, ^2J(P^{M}C) = 11.0 Hz; o-C(PPh$_2$)); 133.6 (dd, ^1J(P^{M}C) = 85.5 Hz, ^3J(P^{A}C) = 4.7 Hz; *i*-C(PPh$_2$)); 134.2 (d, ^4J(P^{X}C) = 3.2 Hz; p-C(PPh$_3$)); 135.1 (d, ^2J(P^{X}C) = 10.3 Hz; o-C(PPh$_3$)); 141.2 (dd, J(PC) = 15.0, 7.6 Hz; C-7a); 145.2 (dd, ^1J(P^{M}C) = 41.7 Hz, ^1J(P^{A}C) = 22 Hz; C-3); 147.2 (ddd, J(PC) = 14.1, 8.9, 2.9 Hz; C-3a); 218.7 (d, ^2J(PC) = 17.8 Hz; CO−Cr−CO); 226.8 (d, ^2J(PC = 10.0 Hz; CO); 230.6 (dd, ^2J(PC) = 8.4, 5.2 Hz; CO). MS ((+)-Xe-FAB, mNBA): *m*/*e* (%): 774 (1) [M$^+$], 718 (100) [M$^+$ − 2 CO], 690 (8) [M$^+$ − 3 CO], 662 (100) [M$^+$ − 4 CO]. IR (CH$_2$Cl$_2$, CaF$_2$): $\bar{\nu}$ = 2010, 1905, 1862 cm^{-1} (νCO).

[Tetracarbonyl-{1-triphenylphosphonio-3-diphenylthioxophosphoranylbenzo[*c*]phospholide-κ^2-*P*,*S*}-tungsten(0)] (10b). [W(CO)$_4$(nbd)] (198 mg, 0.53 mmol) and **9** (220 mg, 0.35 mmol) were reacted as described above to give 238 mg (0.26 mmol, 75%) of **10b**, mp 197 °C (dec). Anal. Calcd for $C_{42}H_{29}WO_4P_3S$ (906.5): C 55.65; H 3.22; S 3.54. Found: C 54.4; H 5.0; S 3.1. ^{1}H NMR: δ 6.52−6.64 (m, 2H; 5-H/6-H), 6.71 (m, 1H; 4-H), 7.00 (m, 1H, 7-H); 7.45 (m, 4H; m-H(PPh$_2$); 7.53 (m, 2H; p-H(PPh$_2$); 7.61 (m, 6H; m-H(PPh$_3$); 7.73 (m, 3H; p-H(PPh$_3$); 7.80 (m, 4H; o-H(PPh$_2$); 7.95 (m, 6H; o-H(PPh$_3$). ^{13}C{^{1}H} NMR: δ 93.6 (dd, ^1J(P^{X}C) = 90.0 Hz, ^1J(P^{A}C) = 32.2 Hz; C-1); 119.3 (m), 119.9 (dd, J(PC) = 4.0, 5.3 Hz), 120.1 (d, J(PC) = 1.6 Hz), 120.8 (s) [C-4 to C-7]; 124.4 (dd, ^1J(P^{X}C = 90.5 Hz, ^3J(P^{A}C) = 2.6 Hz; *i*-C(PPh$_3$)); 129.3 (d, ^{3}J(P^{M}C) = 12.9 Hz; m-C(PPh$_2$)); 130.4 (d, ^3J(P^{X}C) = 12.6 Hz, m-C(PPh$_3$)); 135.1 (d, ^2J(P^{X}C) = 10.3 Hz; o-C(PPh$_3$)), 132.6 (s, p-C(PPh$_2$)); 132.8 (dd, ^1J(P^{M}C) = 85. 2 Hz, ^3J(P^{A}C) = 4.4 Hz; *i*-C(PPh$_2$)); 133.2 (d, ^2J(P^{M}C) = 11.3 Hz; o-C(PPh$_2$)); 134.3 (d, ^4J(P^{X}C) = 3.2 Hz; p-C(PPh$_3$)); 145.4 (m; C-3a/7a); 145.7 (m; C-3a/7a); 201.8 (d, ^2J(P^{A}C) = 10.0 Hz; CO−W−CO); 209.6 (d, ^2J(P^{A}C) = 20.0 Hz; CO); 210.8 (d, ^2J(P^{A}C) = 41.1 Hz; CO). MS ((+)-Xe-FAB, mNBA): *m*/*e* (%) 878 (4) [M$^+$ − CO], 850 (2) [M$^+$ − 2 CO], 794 (12) [M$^+$ − 4 CO]. IR (CH$_2$Cl$_2$, CaF$_2$): $\bar{\nu}$ = 2014, 1902, 1857 cm^{-1} (νCO).

Reaction of 11 with [Cr(CO)$_4$(nbd)]. [Cr(CO)$_4$(nbd)] (90 mg, 0.35 mmol) and **11** (210 mg, 0.35 mmol) were dissolved in 10 mL of THF. After stirring for 4 h, a ^{31}P NMR survey disclosed the presence of approximately 25% (by integration of appropriate signals) of **13a** (cf. Table 1) besides unreacted **11**. Repeated addition of solid [Cr(CO)$_4$(nbd)] increased the yield of **13a**, but led as well to the formation of **6** and small amounts of further unidentified byproducts. The peak yield of **13a** (approximately 70% of phosphorus-containing species) was reached after addition of 10.5 equiv of the chromium complex; a larger excess promoted only further conversion of **13a** into **6**. Attempts to precipitate complex **13a** by addition of hexane during different stages of the reaction yielded product mixtures whose further separation remained unfeasible.

[Tetracarbonyl-{3-(diphenylphosphinylborane)-1-triphenylphosphoniobenzo[*c*]phospholide-κ^2-*P*,*BH*}-tungsten(0)] (13b). [W(CO)$_4$(nbd)] (263 mg, 0.70 mmol) and **11** (210 mg, 0.35 mmol) were dissolved in 10 mL of THF. The solution was stirred for 24 h at room temperature and layered with 10 mL of hexane. A brown precipitate formed that was collected by filtration and dried in a vacuum to give 187 mg (0.21 mmol, 60%) of **13b**, mp 189 °C (dec). Anal. Calcd for

Table 2. Crystallographic Data and Summary of Data Collection and Refinement for 6, 10a,b, and 13b

	6	**10a**	**10b**	**13b**
formula	$C_{43}H_{29}CrO_5P_3-CH_2Cl_2$	$C_{46}H_{37}CrO_5P_3S$	$C_{42}H_{29}O_4P_3SW$	$C_{44.50}H_{32}BO_4P_3W$
fw	855.50	846.73	906.47	918.27
cryst size	0.35 × 0.15 × 0.02 mm	0.18 × 0.05 × 0.02 mm	0.30 × 0.10 × 0.05 mm	0.34 × 0.16 × 0.1 mm
cryst syst, space group	triclinic, $P\bar{1}$ (No. 2)	monoclinic, $P21/c$	monoclinic, Cc (No. 9)	monoclinic, $P21/c$
unit cell dimens	$a = 9.5017(2)$ Å $b = 12.4747(2)$ Å $c = 18.3005(4)$ Å $\alpha = 76.515(1)°$ $\beta = 80.180(1)°$ $\gamma = 74.624(1)°$	$a = 10.9086(2)$ Å $b = 22.0459(5)$ Å $c = 17.3373(3)$ Å $\beta = 101.930(2)°$	$a = 17.8938(5)$ Å $b = 13.2188(3)$ Å $c = 16.4646(4)$ Å $\beta = 106.520(1)°$	$a = 11.06270(10)$ Å $b = 21.8693(2)$ Å $c = 17.3806(2)$ Å $\beta = 102.36°$
volume	2020.15(7) Å^3	4079.39(14) Å^3	3733.69(16) Å^3	4107.41(7) Å^3
Z, ρ_{calc}	2, 1.42 Mg/m^3	4, 1.38 Mg/m^3	4, 1.61 Mg/m^3	4, 1.49 Mg/m^3
μ	0.58 mm^{-1}	0.50 mm^{-1}	3.32 mm^{-1}	2.86 mm^{-1}
F(000)	876	1752	1792	1820
θ range for data collection	2.95 to 25.32°	3.67 to 25.03°	2.58 to 25.00°	3.04 to 27.43°
completeness of data	96.8%			
max. and min. transmn		1.035 and 0.973	0.5444 and 0.4481	1.073 and 0.948
limiting indices	$-11 \le h \le 11$, $-14 \le k \le 15$, $-21 \le l \le 22$	$-12 \le h \le 12$, $-26 \le k \le 26$, $-20 \le l \le 19$	$-21 \le h \le 21$, $-15 \le k \le 15$, $-19 \le l \le 19$	$-14 \le h \le 14$, $-28 \le k \le 28$, $-22 \le l \le 22$
reflections collected/ unique	27 049/7152 [$R_{int} = 0.0372$]	41 298/7154 [$R_{int} = 0.0770$]	38 503/6561 [$R_{int} = 0.0878$]	74 507/9350 [$R_{int} = 0.0541$]
abs corr	none	multiscan	empirical from multiple reflns	multiscan
no. of data/restraints/ params	7152/0/496	7148/0/592	6561/2/461	9350/0/504
goodness-of-fit on F^2	1.065	1.080	0.997	1.081
R1 [$I > 2\sigma(I)$]	0.037	0.048	0.034	0.027
wR2 (all data)	0.010	0.117	0.073	0.069
largest diff. peak and hole	0.352 and −0.391 e Å^{-3}	0.574 and −0.418 e Å^{-3}	0.662 and −1.424 e Å^{-3}	0.833 and −1.153 e Å^{-3}

$C_{42}H_{32}BO_4P_3W$ (888.3): C 56.79; H 3.63. Found: C 56.8; H 3.9. ^{1}H NMR: δ −1.33 (br, 3H; BH_3); 6.45 (m, 1H; 4-H/7-H); 6.52 (m, 1H; 5-H/6-H); 6.65 (m, 1H; 5-H/6-H), 7.06 (m, 1H, 4-H/7-H); 7.43 (m, 6H; m-H(PPh_3); 7.57−7.76 (m, 13H; C_6H_5); 8.00 (m, 6H; o-H(PPh_3). ^{11}B NMR: δ −40.3 (br). ^{13}C{^{1}H} NMR: δ 118.0 (dd, J(PC) = 6.5, 3.6 Hz; C-6); 118.7 (ddd, J(PC) = 11.0, 1.5, 1.4 Hz; C-5/6); 119.0 (d, J(PC) = 2.3 Hz; C-4/7); 119.1 (s; C-4/7); 123.7 (dd, $^1J(P^XC)$ = 90.5 Hz, $^3J(P^AC)$ = 2.3 Hz; i-C(PPh_3)); 128.2 (d, $^3J(P^MC)$ = 10.6 Hz; m-C(PPh_2)); 128.8 (dd, $^1J(P^MC)$ = 64.1 Hz, $^3J(P^AC)$ = 7.6 Hz; i-C(PPh_2)); 129.0 (d, $^3J(P^XC)$ = 12.9 Hz; m-C(PPh_3)); 130.4 (d, $^2J(P^MC)$ = 2.9 Hz; p-C(PPh_2)); 132.3 (d, $^2J(P^MC)$ = 9.7 Hz; o-C(PPh_2)); 133.0 (d, $^4J(P^XC)$ = 3.0 Hz; p-C(PPh_3)); 134.0 (d, $^2J(P^XC)$ = 10.3 Hz; o-C(PPh_3)); 141.9 (dd, J(PC) = 15.2, 2.9 Hz; C-3a/7a); 144.7 (dd, J(PC) = 14.5, 5.9 Hz; C-3a/7a); 200.5 (d, ^2J(PC) = 10.3 Hz; CO−Cr−CO); 204.7 (d, ^2J(PC = 5.2 Hz; CO); 206.8 (d, ^2J(PC) = 36.3 Hz; CO). ^{183}W NMR: δ −2858. MS ((+)-Xe-FAB, mNBA): m/e (%) 860 (16) [M$^+$ − CO], 846 (9) [M$^+$ − CO, − BH_3], 818 (4) [M$^+$ − 2 CO, − BH_3]. IR (CH_2Cl_2, CaF_2): $\bar{\nu}$ = 2380, 2340 (sh) cm^{-1}, (νBH); 1980, 1925, 1867 cm^{-1} (νCO).

Crystallography. Crystals of composition **6**·CH_2Cl_2, **10a**·THF, **10b**, and **13b**·0.5toluene were obtained from CH_2Cl_2/THF and toluene/THF, respectively. The crystal structure determinations were performed on a Nonius KappaCCD diffractometer at 123(2) K (for **6**, **10b**) or 223(2) K (for **10a**, **13b**) using Mo Kα radiation (λ = 0.71073 Å). Crystal data, data collection parameters, and results of the analyses are listed in Table 2. The structures were solved by direct methods (SHELXS-97[15a]) and refined anisotropically by blocked cycle full-matrix least-squares on F^2 using all data (SHELXL-97[15b]) using an empirical absorption correction from multiple reflections (**10b**), or multiscan absorption corrections (**6**, **10a**, **13b**). The BH atoms in **13b** were located and refined isotropically; all remaining H atoms were refined with a riding model. The crystal of **10b** was a racemic twin and gave an absolute structure parameter of 0.362(7). The solvent molecule (toluene) in the structure of **13b**·0.5toluene was disordered.

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Supporting Information Available: Expansion of the ^{1}H NMR spectrum of **13b** under different decoupling conditions; tables of atom parameters, anisotropic temperature factors, and bond distances and angles for **6**·CH_2Cl_2, **10a**·THF, **10b**, and **13b**·0.5toluene. This material is available free of charge via the Internet at http://pubs.acs.org.

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[15] (a) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467. (b) Sheldrick, G. M. *SHELXL-97*; University of Göttingen, 1997.