Terminal Carbido Complexes of Osmium: Synthesis, Structure, and Reactivity Comparison to the Ruthenium Analogues

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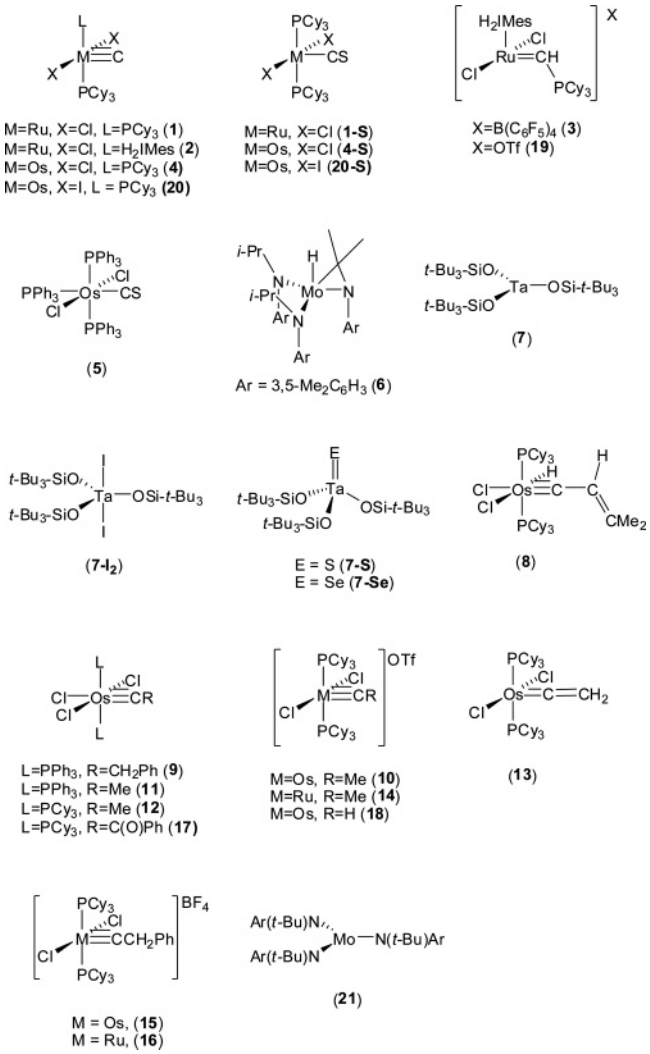
The first terminal carbide complex of osmium, $Os(\equiv C)(PCy_3)_2Cl_2$ (**4**), was synthesized via S-atom abstraction from $Os(CS)(PCy_3)_2Cl_2$ (**4-S**) by $Ta(OSi\text{-}t\text{-}Bu_3)_3$ (**7**). Compound **4** reacts with HO_3SCF_3 (HOTf) to form the first cationic osmium methylidyne complex $[Os(\equiv CH)(PCy_3)_2Cl_2][OTf]$ (**18**). The analogous ruthenium complex $[Ru(\equiv CH)(H_2IMes)(PCy_3)Cl_2][OTf]$ is not observed upon protonation of $Ru(\equiv C)(H_2IMes)(PCy_3)Cl_2$ (**2**) with HOTf. Substitution of the chloride ligands in **4** is surprisingly difficult compared to the case of **4-S**, but $Os(\equiv C)(PCy_3)_2I_2$ can be obtained. Compound **4** also reacts with a variety of electrophiles to afford cationic five-coordinate and neutral six-coordinate carbyne complexes. In general, **4** reacts more readily with electrophiles than does **1**, and cationic carbyne complexes formed from **4** are more resistant to degradation than are their Ru counterparts.

Introduction

The chemistry of carbide ligands is of interest for several reasons. In the area of heterogeneous catalysis, surface-bound carbides are thought to serve as critical intermediates in the Fischer−Tropsch and related processes for catalytic formation of hydrocarbons and "oxygenates" from synthesis gas.[1−7] Carbides are also important to homogeneous catalysis, particularly olefin metathesis catalyzed by ruthenium complexes. For example, a bridging carbido complex is formed upon decomposition of $Ru(=CH_2)(H_2IMes)(PCy_3)Cl_2$, a commonly used catalyst for ring-closing metathesis (RCM) of olefins.[8] In many cases, the decomposition products of Grubbs-type catalysts are not yet known, but in a growing number of examples the terminal carbide complexes exemplified by $Ru(\equiv C)(L)(PCy_3)Cl_2$ (L = PCy_3 [**1**], H_2IMes [**2**]; see Chart 1) are formed cleanly.[9−14] The marked stability[9,10,15] of **1** and **2** is surprising given the general rarity of terminal carbide complexes.[9,10,16−19] Compounds **1** and **2** are important not only as catalyst

Chart 1. Numbered Compounds



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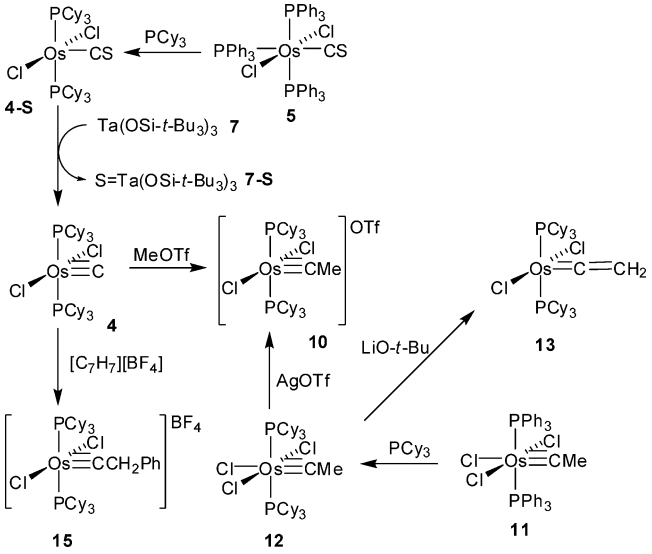
Scheme 1. Synthesis and Reactivity of 4 with Electrophiles



decomposition products to be avoided but also as precursors to active olefin metathesis catalysts via protonation of the carbide ligand and rearrangement to afford phosphoniocarbene complexes that initiate metathesis of terminal olefins rapidly.[19] As four-coordinate 14-electron complexes, phosphoniocarbene **3** (Chart 1) and a closely related complex have been particularly useful in establishing the structure and dynamics of the ruthenacyclobutane intermediates in olefin cross-metathesis.[20,21]

In order to gain additional insight into the factors that govern the stability and reactivity of terminal carbide complexes such as **1** and **2**, we sought to make the osmium analogue Os(≡C)-$(PCy_3)_2Cl_2$ (**4**) for comparison to compounds based on ruthenium. Herein we report the synthesis, structure, and reactions of **4**, including its protonation to form a terminal methylidyne complex. Compound **4** is the first terminal carbide complex of any metal other than Mo, W, and Ru and the first neutral terminal carbide complex that does not contain Ru; the unstable cationic methylidyne complex formed by protonation of **4** is the first terminal methylidyne complex isolated for any metal other than Mo and W.[22]

Results and Discussion

We recently showed that **1** can be formed by S-atom abstraction from its thiocarbonyl homologue.[10] Complex **1** is quite stable. It does not react with air, water, or benzoic acid. In fact, the only reactions it is reported to undergo are its transformation into $Ru(CO)(PCy_3)_2Cl_2$ and $Ru(CS)(PCy_3)_2Cl_2$ (**1-S**),[10] its protonation to yield $[Ru(=CHPCy_3)(PCy_3)Cl_2][BX_4]$ ($X = F$, C_6F_5),[19] the formation of weak complexes with the $Mo(CO)_5$ and $Pd(Cl)_2(SMe_2)$ fragments,[15] and [2+1] cycloaddition with activated alkynes to afford cyclopropenylidene complexes.[23]

Unlike the case for ruthenium,[10] the lack of a suitable metathesis-active precursor prevented us from preparing **4** via metathesis of an alkylidene complex with Feist's ester or a vinyl ester. We circumvented this complication by employing desulfurization of the thiocarbonyl analogue $Os(CS)(PCy_3)_2Cl_2$ (**4-S**) to obtain **4** (Scheme 1). Complex **4-S** is prepared in 53% yield from known $Os(CS)(PPh_3)_3Cl_2$ (**5**)[24] upon phosphine exchange using PCy_3.

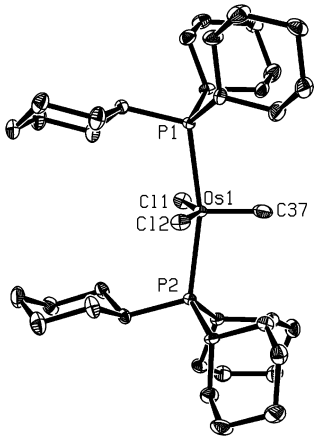


Figure 1. 50% thermal ellipsoid plot of **4**.

We next subjected **4-S** to the conditions for S-atom abstraction that effect the conversion of **1-S** into **1**.[10] Reaction of **4-S** with 3 equiv of $Mo(H)(\eta^2\text{-}Me_2CNAr)(N[i\text{-}Pr]Ar)_2$ (Ar = 3,5-$Me_2C_6H_3$) (**6**)[25] for 5 h in C_6D_6 at 28 °C results in clean conversion of **4-S** into **4**. The usual molybdenum-containing byproduct, $(\mu\text{-}S)(Mo(N[i\text{-}Pr]Ar)_3]_2$,[10] is also observed by ^1H NMR spectroscopy. $^{13}C\{^1H\}$ NMR spectroscopy reveals the signal for the terminal carbido ligand in **4** at 448 ppm, a shift diagnostic of a terminal carbido species.[9,10,16−19] Unlike **1**, however, **4** appears to decompose during workup. Accordingly, we investigated other potential S-atom abstractors. We find that $Ta(OSi\text{-}t\text{-}Bu_3)_3$ (**7**)[26] reacts cleanly with **4-S** in toluene over 49 h at room temperature to produce a 1:1 mixture of **4** and the terminal sulfide complex $S{=}Ta(OSi\text{-}t\text{-}Bu_3)_3$ (**7-S**),[27] which is readily separated from **4** by extraction with pentane following removal of the toluene solvent (Scheme 1). This afforded pure **4** in 89% yield. As expected, addition of elemental sulfur to a solution of **4** in C_6D_6 affords quantitative regeneration of **4-S**.

The structure of **4** (Figure 1) was determined by single-crystal X-ray diffraction in order to confirm its identity as a monomeric terminal carbido complex and to establish its coordination geometry. Crystals were grown by slow diffusion of pentane into a dichloromethane solution of **4**. Acquisition and refinement data for **4**, **4-S**, and **15** are summarized in Table 1. Pertinent bond lengths and angles for **4**, **4-S**, and **15** are listed in Table 2 for comparison to those of the ruthenium complexes **1**[15] and **1-S**.[10] Compound **4** crystallizes in the space group $P2(1)/c$ as a discrete neutral species. As was the case for **1**, the carbido ligand occupies the apical position in what is best described as a square pyramid ($\tau = 0.17$[28]). The Os−C interatomic distance of 1.689(5) Å is consistent with a short triple bond. For comparison, the Os−C bond lengths in the carbyne complexes $[Os(\equiv CCH{=}CMe_2)(PCy_3)_2HCl_2]$ (**8**) and $[Os(\equiv CCH_2Ph)(PPh_3)_2Cl_3]$ (**9**) are

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Table 1. Crystallographic Data

	4-S·$(CH_2Cl_2)_2$	**4**	**15**·(CH_2Cl_2)
crystals grown by	cooling a conc CH_2Cl_2 solution to −35 °C	slow diffusion of pentane into a CH_2Cl_2 solution	slow diffusion of pentane into a CH_2Cl_2 solution
cryst color, habit	green, block	orange, plates	pale green, plates
formula	$C_{39}H_{70}Cl_6P_2SOs$	$C_{37}H_{66}Cl_2P_2Os$	$C_{45}H_{75}BCl_4F_4P_2Os$
fw	1035.85	833.94	1096.80
cryst size (mm)	0.50 × 0.48 × 0.46	0.18 × 0.10 × 0.10	0.44 × 0.24 × 0.12
a (Å)	11.7573(6)	13.1464(12)	12.268(3)
b (Å)	14.4579(7)	23.313(2)	14.927(3)
c (Å)	15.3416(8)	13.5957(12)	14.950(3)
α (deg)	95.308(2)	90	114.796(2)
β (deg)	112.333(2)	115.585(5)	105.238(3)
γ (deg)	105.071(2)	90	91.668(3)
V (Å^3)	2275.2(2)	3758.2(6)	2367.4(9)
Z	2	4	2
D_{calcd} (Mg m^{-3})	1.512	1.474	1.539
μ_{calcd} (mm^{-1})	3.297	3.645	3.034
cryst syst	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2(1)/n$	$P\bar{1}$
T (K)	123(2)	123(2)	123(2)
θ range (deg)	1.90 ≤ *θ* ≤ 28.32	1.75 ≤ *θ* ≤ 27.47	1.96 ≤ *θ* ≤ 28.32
hkl range	−15 ≤ *h* ≤ 14 −19 ≤ *k* ≤ 19 −20 ≤ *l* ≤ 20	−16 ≤ *h* ≤ 15 −30 ≤ *k* ≤ 30 −17 ≤ *l* ≤ 17	−16 ≤ *h* ≤ 16 −19 ≤ *k* ≤ 19 −19 ≤ *l* ≤ 19
no. of reflections			
collected	74 381	129 783	75 165
unique	11 287	8526	11 718
no. of params/restraints	442/0	379/0	514/0
GOF	1.078	1.127	1.089
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0163 wR2 = 0.0422	R1 = 0.0337 wR2 = 0.0716	R1 = 0.0333 wR2 = 0.0857

Table 2. Selected Bond Lengths (Å) and Angles (deg), Structural Comparison of 1, 1-S, 4, 4-S, and 15

	1[15]	**1-S**[10]	**4**	**4-S**	**15**
[M−C]	1.632(6)	1.7376(19)	1.689(5)	1.7579(17)	1.701(3)
[M−P][a]	2.427(2)	2.418(1)	2.415(2)	2.4097(6)	2.452(1)
[M−Cl][a]	2.376(2)	2.369(1)	2.372(2)	2.3734(6)	2.343(1)
[P−M−P]	160.66(5)	165.789(18)	165.71(4)	165.196(14)	161.68(3)
[Cl−M−Cl]	156.66(5)	166.290(19)	155.46(4)	163.823(15)	156.16(3)

[a] Average values.

1.715(4) and 1.734(3) Å, respectively.[29,30] Benzylidyne complexes display similar Os≡C bond lengths.[31−36]

Single-crystal X-ray diffraction reveals that **4-S** has a structure grossly similar to that of **4** (Figure 2, Tables 1, 2). Compound **4-S** crystallizes from cooled dichloromethane as a monomer in the space group $P\bar{1}$. Compared to **4**, the Os−C bond in **4-S** is considerably longer. The P−Os−P bond angle in **4-S** is essentially unchanged from that in **4** (Table 2). In contrast, the Cl−Os−Cl bond angle is over 8° larger in **4-S** than in **4**; consequently, **4-S** is even closer to the limiting square-pyramidal structure ($\tau = 0.02$[28]). The thiocarbonyl ligand occupies the apical site. In spite of the fact that halide exchange is more rapid in **4-S** than in **4**, the difference in mean Os−Cl bond lengths between these two complexes is statistically insignificant. The difference in mean Os−P bond lengths between complexes **4-S** and **4** is also statistically insignificant. The same trend is seen for Ru (Table 2).

It is also instructive to compare these metrical parameters to those of **1**[15] and **1-S**[10] (Table 2). The mean Os−Cl bond length in **4** is indistinguishable from that of its Ru counterpart, **1**. The mean Os−P bond length in **4** is slightly shorter than the mean Ru−P internuclear distance in **1**. Similarly, the mean M−Cl and M−P bond lengths in **4-S** are statistically indistinguishable from those of its Ru analogue, **1-S**. Unlike the case of the osmium complexes (*vide supra*), upon S-atom abstraction from **1-S**, both the P−Ru−P and the Cl−Ru−Cl bond angles decrease. The structures are otherwise very similar; the largest differences in bond lengths occur for the M−C bonds in both **1**/**4** and **1-S**/**4-S**. Although the Ru−C bond in **1-S** is already shorter than the Os−C bond in **4-S**, upon desulfurization the Ru−C internuclear separation decreases even more than does the Os−C distance.

Reactions with Alkylating Agents. Although **4** does not react with air or water at room temperature, it is somewhat more Lewis basic than is **1**. Addition of MeOTf (Tf = CF_3SO_2) to a CD_2Cl_2 solution of **4** at −35 °C followed by warming to 28 °C affords the cationic five-coordinate ethylidyne complex [Os(≡CMe)$(PCy_3)_2Cl_2$][OTf] (**10**) cleanly in 20.5 h (Scheme 1). In order to confirm the identity of this new compound, we synthesized it independently from known Os(≡CMe)$(PPh_3)_2Cl_3$ (**11**)[30] via phosphine exchange with 3.4 equiv of PCy_3 in

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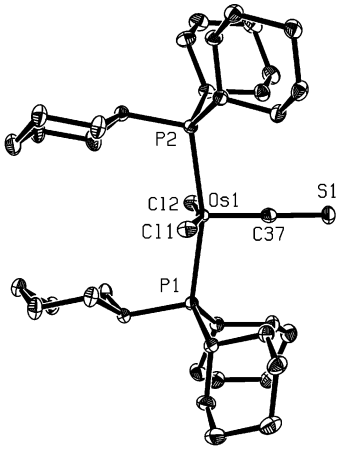


Figure 2. 50% thermal ellipsoid plot of **4-S**.

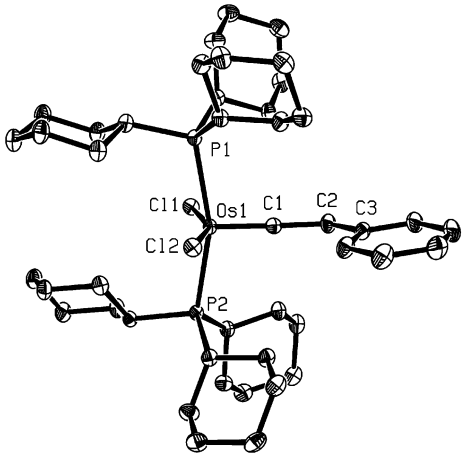
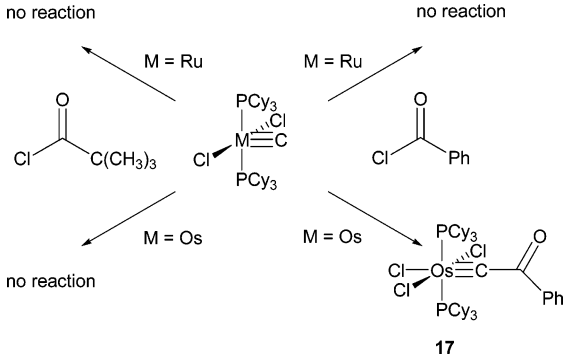


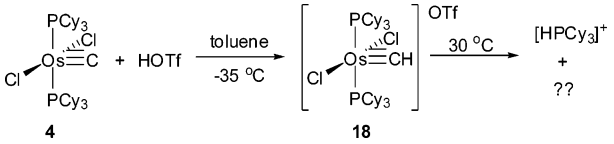
Figure 3. 50% thermal ellipsoid plot of **15** (BF_4^- counterion not shown).

refluxing THF for 1.2 h, followed by treatment with 1 equiv of AgOTf in CH_2Cl_2. The intermediate complex Os(≡CMe)-$(PCy_3)_2Cl_3$ (**12**) was isolated in 64% yield after recrystallization from dichloromethane. Following the reaction with AgOTf, pure **10** was isolated in 67% yield from **12** by this route. Like similar complexes,[29,37−41] **12** is readily deprotonated to form the analogous vinylidene[42−48] complex. Treatment of **12** with 1.1 equiv of LiO-*t*-Bu in THF afforded vinylidene **13** in 59% yield after recrystallization (Scheme 1). In contrast, reaction of **1** with MeOTf affords an unstable intermediate that appears by multinuclear NMR spectroscopy to be the corresponding cationic ethylidyne complex, [Ru(≡CMe)$(PCy_3)_2Cl_2$][OTf] (**14**). However, this compound is difficult to isolate in pure form because it slowly decomposes in solution, affording $[HPCy_3]^+$ and uncharacterized ruthenium product(s). Werner has similarly noted the instability of cationic complexes of the form [Ru(≡CCH_2R')$(PR_3)_2Cl_2]^+$ (R′ = Ph, *t*-Bu; R = *i*-Pr, Cy) with respect to formation of $[HPR_3]^+$ in solution.[37] Related cationic carbyne-hydride complexes[29,39,49] can also decompose by deprotonation.

Scheme 2. Reactivity of 1 and 4 with Acylating Agents



Scheme 3. Protonation of 4



Both **4** and **1** react cleanly with $[C_7H_7][BF_4]$ to afford the cationic alkylidyne complexes [M(≡CCH_2Ph)$(PCy_3)_2Cl_2][BF_4]$ (M = Os [**15**], Ru [**16**]) following spontaneous ring contraction. Single-crystal X-ray diffraction was employed in order to confirm the identity of **15** (Tables 1, 2). A thermal ellipsoid plot (Figure 3) of the cation evinces the expected connectivity, a square-pyramidal coordination geometry about Os, and an Os≡C triple bond. The Os≡C bond length of 1.701(3) Å in **15** is similar to those found in **4**, **8**, and **9**. Unlike **14**, crude **16** was initially isolated without significant decomposition to $[HPCy_3]^+$. However, crude **16** partially decomposed under the conditions of attempted recrystallization, yielding $[HPCy_3]^+$ and uncharacterized ruthenium products.

Reactions with Acylating Agents. In analogous fashion to its reactions with alkylating agents, **4** reacts cleanly with benzoyl chloride, forming the six-coordinate acylcarbyne complex Os-(≡CC(O)Ph)$(PCy_3)_2Cl_3$ (**17**) in 88% isolated yield (Scheme 2). Complex **4** does not react at all with pivaloyl chloride under these conditions, probably for steric reasons. Unlike **4**, compound **1** does not react with either of these acylating agents under these conditions. This highlights a small but important difference in the Lewis base strengths of **1** and **4**.

Reaction with Strong Acids. As noted earlier, **1** and **2** react with the strong acids HBX_4 (X = F, C_6F_5) to afford cationic phosphoniomethylidene complexes via an apparent 1,2-migration of the PCy_3 ligand following protonation of the carbide ligand. The mechanism of this transformation has not yet been determined. Protonation of **4** with these acids has to date failed to yield tractable products. However, reaction of **4** with trifluoromethanesulfonic acid (HOTf) in toluene at −35 °C produced [Os(≡CH)$(PCy_3)_2Cl_2$][OTf] (**18**) as an insoluble pale tan compound that decomposes slowly when dissolved in CH_2Cl_2 (Scheme 3). Over a period of 8 h at room temperature, 97%

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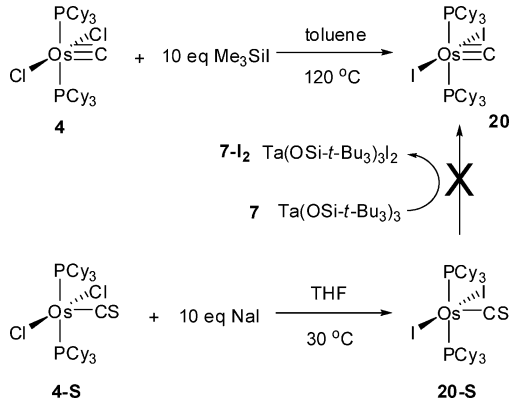
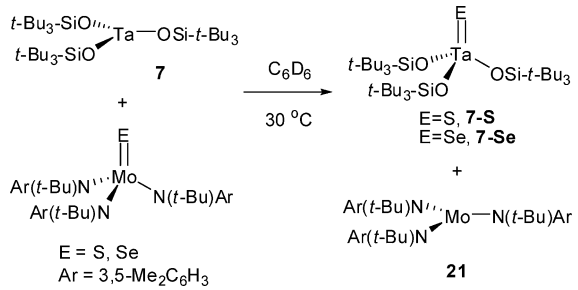
Scheme 4. Synthetic Routes to 20



Scheme 5. Intermetal Atom Transfer



decomposition of **18** to form multiple products was observed. This is in contrast to the case of protonation of related **2** by HOTf, which yields the phosphoniocarbene complex **19** cleanly without observation of any intermediate even at −80 °C.[14] The greater osmium−ligand bond strength compared to the ruthenium−ligand bond strength in homologous complexes likely accounts for the observed preference for a structure with more metal−ligand bonds in the case of Os.

Substitution of Ancillary Halide Ligands. Substitution of the chloride ligands in **1** is notoriously difficult compared to halide substitution in its precursors.[10,50,51] This is also the case for **4**. As we desired the diiodide analogue of **4**, Os(≡C)-$(PCy_3)_2I_2$ (**20**), for ongoing reactivity studies, we examined its synthesis by several routes. Although the process is slow, direct conversion of **4** into **20** can be achieved in low isolated yield (28%) by heating a toluene solution of **4** and 10 equiv of Me_3-SiI to 120 °C for 10 h in a sealed vessel (Scheme 4). The low yield results primarily from difficulty in separating an impurity, not poor conversion. Nevertheless, this is the preferred method for generating **20**, rather than S-atom abstraction from Os(CS)-$(PCy_3)_2I_2$ (**20-S**), as explained next. Crude **20-S** can be prepared in 85% yield from **4-S** by reaction with 10 equiv of NaI in THF for 24 h at 30 °C and subsequently purified by two consecutive crystallizations from dichloromethane at −35 °C. Unfortunately, reaction of **20-S** with **7** in C_6D_6 results in double iodine-atom abstraction, affording Ta(OSi-*t*-$Bu_3)_3I_2$ (**7-I$_2$**)[52] as the principal Ta-containing product. Although reaction of **20-S** with **6** in C_6D_6 produces **20**, the reaction is not clean, and several unidentified P-containing products are also formed. Furthermore, we were unable to separate **20** from the Mo-containing byproduct, (μ-S)(Mo(N[*i*-Pr]Ar)$_3$]$_2$, because of their very similar solubilities.

Comparison of Ta(III) and Mo(III) Complexes as Chalcogen Atom Abstractors. Neither **6** nor **7** emerged as a generally superior S-atom abstractor in these studies. Instead, each is preferred under certain circumstances. Nevertheless, the intermetal chalcogen atom-transfer reactions shown in Scheme 5 confirm the expectation that **7** is thermodynamically superior to **21** (which should be comparable to **6**)[53] as a S-/Se-atom abstractor.

Conclusions

In summary, we have prepared a unique terminal osmium carbide complex, **4**, via S-atom abstraction from the thiocarbonyl analogue **4-S** using a Ta(III) reagent, **7**. Compound **7** is thermodynamically superior to the masked Mo(III) compound **6** that had previously been used to generate carbide complexes via S-atom abstraction. However, **6** is more tolerant of heavier halides in the ancillary ligand set than is **7**. Single-crystal X-ray diffraction reveals that molecular **4** adopts an approximately square-pyramidal core geometry, with the carbido ligand occupying the apical position and a short Os≡C bond. Air-stable **4** is somewhat more Lewis basic than its Ru homologue **1**, forming stable alkylidyne complexes upon reaction with a variety of electrophiles; the corresponding cationic carbyne complexes are more persistent for Os than for Ru. We are currently investigating the reactivity of **4** and some analogues prepared from it by substitution of the ancillary ligand set toward a number of other electrophiles, oxidants, and reductants. We are also exploring the further reactions of the unstable cationic terminal methylidyne complex (**18**) that is formed upon protonation of **4** by trifluoromethanesulfonic acid. The formation of cationic **18** illustrates a key divergence in the chemistry of the ruthenium carbide **1** from that of the osmium carbide **4** upon protonation.

Experimental Section

General Procedures. All reactions were carried out using standard Schlenk techniques under an atmosphere of nitrogen or in a nitrogen-filled MBraun Labmaster 130 glovebox, unless otherwise specified. ^{1}H, ^{13}C, ^{31}P, and ^{19}F NMR spectra were recorded on a Varian Inova 300 MHz or 400 MHz spectrometer. ^{1}H and ^{13}C NMR spectra were referenced to solvent signals.[54] ^{19}F NMR spectra were referenced to external $CFCl_3$ in $CDCl_3$ (δ = 0). ^{31}P NMR spectra were referenced to external 85% aqueous H_3PO_4 (δ = 0).

Materials. All solvents were dried by passage through solvent purification columns according to the method of Grubbs.[55] Deuterated solvents were dried over 4 Å molecular sieves. Silver trifluoromethanesulfonate, iodomethane, trifluoromethanesulfonic acid, methyl trifluoromethanesulfonate, sodium iodide, iodotrimethylsilane, and pivaloyl chloride were purchased from Acros. Sulfur was purchased from Mallinckrodt. Tricyclohexylphosphine was purchased from Organometallics Inc. Tropylium tetrafluoroborate was purchased from Matrix Scientific. Lithium *tert*-butoxide was purchased from Strem. Benzoyl chloride was purchased from Alfa Aesar. Selenium powder (~100 mesh) was purchased from Aldrich. Solid and liquid reagents were used as received. Ta(OSi-*t*-$Bu_3)_3$ (**7**),[26] Os(CS)$(PPh_3)_3Cl_2$ (**5**),[24] Os(≡CMe)$(PPh_3)_2Cl_3$ (**11**),[30]

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Mo(H)(η^2-Me_2CNAr)(N[*i*-Pr]Ar)$_2$ (**6**),[25] S═Mo(N[*t*-Bu]Ar)$_3$,[56] and Se═Mo(N[*t*-Bu]Ar)$_3$[56] were synthesized according to published procedures.

Synthetic Procedures. [Os(CS)(PCy_3)$_2$$Cl_2$] (4-S). Method A (preparative scale). The crude residue from a preparation of **5** (3.03 g, 2.77 mmol) was dissolved without purification in dichloromethane (230 mL). Tricyclohexylphosphine (3.89 g, 13.9 mmol, 5.02 equiv) was added to the dichloromethane solution. The mixture was stirred for 1.2 h at 30 °C, and then the solvent was removed under vacuum. The resulting brown solid was slurried in a mixture of diethyl ether (5 mL) and pentane (25 mL), stirred for 20 min, filtered, washed with pentane (20 mL), and then washed with diethyl ether (3 × 10 mL). The brown powder was dissolved in minimal dichloromethane (60 mL), and tricyclohexylphosphine (2.19 g, 7.81 mmol) was added to the solution. The mixture was stirred for 30 min at 30 °C, and then the solvent was removed under vacuum. The resulting brown powder was slurried in pentane (20 mL) and diethyl ether (10 mL), stirred for 30 min, filtered, washed with pentane (3 × 10 mL), washed with diethyl ether (3 × 10 mL), and then dried *in vacuo*. Crude brown **4-S** was dissolved in dichloromethane (26 mL) and placed in the freezer overnight at −35 °C, whereupon green crystals of [**4-S**·(CH_2Cl_2)$_2$] formed. The crystals were filtered, washed with cold dichloromethane (3 × 5 mL), and dried under vacuum. The crystals rapidly converted to a green powder upon drying. A second crop was recovered from the filtrate in a similar manner, resulting in 1.27 g (1.47 mmol, 53.1%) of green **4-S**. This green powder was lyophilized from benzene to remove residual dichloromethane to yield pure **4-S**. ^{1}H NMR (CD_2Cl_2): δ 2.97 (m, 6H, P(C_6H_{11})$_3$), 2.11 (pseudo-d, 12H, P(C_6H_{11})$_3$), 1.84 (m, 12H, P(C_6H_{11})$_3$), 1.74 (br s, 6H, P(C_6H_{11})$_3$), 1.55 (pseudo-q, 12H, P(C_6H_{11})$_3$), 1.26 (m, 18H, P(C_6H_{11})$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 239.68 (t, $^2J_{PC}$ = 6 Hz, Os(CS)), 33.80 (virtual t, $^1J_{PC}$ = 12 Hz, P(C_6H_{11})$_3$), 30.42 (s, P(C_6H_{11})$_3$), 28.38 (virtual t, $^2J_{PC}$ = 5 Hz, P(C_6H_{11})$_3$), 27.05 (s, P(C_6H_{11})$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2): 18.3 (s). Anal. Calcd for $C_{37}H_{66}Cl_2P_2SOs$: C, 51.31; H, 7.68. Found: C, 51.43; H, 7.39.

Method B (NMR scale). Compound **4** (0.0083 g, 0.010 mmol) and S_8 (0.0014 g, 0.0055 mmol) were dissolved in C_6D_6 (0.8 mL) and stirred at 30 °C. Reaction progress was monitored for the disappearance of starting material (δ 23.3) and the appearance of product (δ 18.3) by ^{31}P NMR spectroscopy. Clean conversion to product required 24 h.

[Os(≡C)(PCy_3)$_2$$Cl_2$] (4). Method A. Green-yellow, powdery **4-S** (1.18 g, 1.36 mmol) was dissolved in toluene (40 mL). Separately, blue, crystalline Ta(OSi-*t*-Bu_3)$_3$ (1.28 g, 1.55 mmol, 1.14 equiv) was dissolved in toluene (40 mL), poured into the solution of **4-S**, and rinsed in with an additional 10 mL of fresh toluene. The flask was evacuated, sealed, and stirred overnight at 30 °C. Reaction progress was monitored for disappearance of starting material (δ 18.4) relative to appearance of **4** (δ 23.4) by ^{31}P NMR spectroscopy. After stirring for 24 h, a ^{31}P NMR spectrum showed 95% conversion to **4**. Compound **7** (71 mg, 0.086 mmol, 0.063 equiv) was added to the toluene solution, stirred for 3 h, and analyzed by ^{31}P NMR spectroscopy. No change was observed by NMR spectroscopy. Additional **7** (71 mg, 0.086 mmol, 0.063 equiv) was added to the toluene solution and stirred for 22 h at 30 °C. ^{31}P NMR spectroscopy showed complete conversion of **4-S** to **4**. The solvent was removed under vacuum, and the resulting brown solid was slurried in pentane (20 mL), filtered, washed with 10 mL of pentane, washed with additional pentane (4 × 5 mL), and then dried *in vacuo*, affording pure **4** as a pale yellow powder (1.01 g, 1.21 mmol, 89.4%). ^{1}H NMR (C_6D_6): δ 2.91 (m, 6H, P(C_6H_{11})$_3$), 2.41 (pseudo-d, 12H, P(C_6H_{11})$_3$), 1.72 (m, 24H, P(C_6H_{11})$_3$), 1.59 (m, 6H, P(C_6H_{11})$_3$), 1.20 (m, 18H, P(C_6H_{11})$_3$). ^{13}C{^{1}H} NMR (C_6D_6): δ 448.45 (s, Os(C)), 31.51 (virtual t, $^1J_{PC}$ = 12 Hz, P(C_6H_{11})$_3$), 30.09 (s, P(C_6H_{11})$_3$), 28.29 (virtual t, $^2J_{PC}$ = 5 Hz, P(C_6H_{11})$_3$), 27.12 (s, P(C_6H_{11})$_3$). ^{31}P-{^{1}H} NMR (C_6D_6): 23.39 (s). Anal. Calcd for $C_{37}H_{66}Cl_2P_2Os$: C, 53.28; H, 7.98. Found: C, 53.38; H, 7.95.

Method B. 4 was synthesized from **4-S** and **6**. Compound **4-S** (0.323 g, 0.373 mmol) was dissolved in benzene (50 mL). Solid **6** (0.611 g, 1.05 mmol, 2.82 equiv) was added to the benzene solution with stirring, and the reaction mixture was sealed under vacuum. The reaction was monitored by ^{31}P NMR spectroscopy. The mixture was stirred for 2 h at 30 °C, and then more **6** (0.130 g, 0.223 mmol, 0.598 equiv) was added. After 14 h, ^{31}P NMR spectroscopy showed complete consumption of the starting material and one peak corresponding to the carbido product **4** (δ 23.5). The mixture was frozen in benzene at −35 °C and lyophilized, affording a black-brown residue. The remaining residue was washed with cold pentane (2 × 20 mL, then 4 × 5 mL). The filtrate was analyzed by ^{31}P NMR spectroscopy and showed three peaks: δ 36.4 (unassigned, 8.0%), 23.5 (**4**, 38.5%), and 10.6 (PCy_3, 53.5%). The remaining solid was washed with cold diethyl ether (4 × 5 mL). The filtrate was analyzed by ^{31}P NMR spectroscopy and showed one peak corresponding to **4**; the mass was small and not quantified. No ^{31}P NMR signal was observed in the ^{31}P NMR spectrum of the remaining solid. The ^{1}H NMR spectrum identified the remaining material as a mixture of (μ-N)[Mo(N[*i*-Pr]Ar)$_3$]$_2$ and (μ-S)[Mo(N[*i*-Pr]Ar)$_3$]$_2$.

[Se═Ta(OSi-*t*-Bu_3)$_3$] (7-Se). Selenium (9.7 mg, 0.12 mmol, 1.0 equiv) was added to a stirred, blue solution of compound **7** (101 mg, 0.122 mmol) in diethyl ether (5 mL) at 30 °C. The blue solution bleached within 1 min, leaving a nearly colorless solution with a faint yellow tint. The mixture was stirred for 30 min and filtered, and then the solvent was removed under reduced pressure. The white residue was dissolved in minimal pentane and cooled to −35 °C overnight. The fine white needles that formed were filtered on a cold frit, washed with cold pentane (3 × 2 mL), and dried *in vacuo*. A second crop was collected in a similar manner, yielding **7-Se** (22 mg, 0.024 mmol, 20%). ^{1}H NMR (C_6D_6): δ 1.32 (s). ^{13}C{^{1}H} NMR (C_6D_6): δ 30.66 (s, C(*C*H$_3$)$_3$), 24.03 (s, *C*(CH$_3$)$_3$). Anal. Calcd for $C_{36}H_{81}O_3SeSi_3Ta$: C, 47.71; H, 9.01. Found: C, 48.09; H, 9.34.

[Os(≡CMe)(PCy_3)$_2$$Cl_2$][OTf] (10). Method A (preparative scale). Compound **12** (0.121 g, 0.137 mmol) was dissolved in dichloromethane (10 mL) in a vial covered with black electrical tape. Silver trifluoromethanesulfonate (36 mg, 0.14 mmol, 1.0 equiv) was added to the dichloromethane solution of **12**. The mixture was stirred for 30 min and then filtered through a bed of Celite with dichloromethane. The solvent was removed under vacuum, and the residue was dried *in vacuo* overnight. The orange-brown residue was suspended in diethyl ether (5 mL), stirred for 5 min, filtered, washed with diethyl ether (2 × 3 mL), and dried *in vacuo*, affording pure light tan **10** (91 mg, 0.091 mmol, 67%). ^{1}H NMR (CD_2Cl_2): δ 3.02 (m, 6H, P(C_6H_{11})$_3$), 2.22 (s, 3H, CH_3), 1.93 (m, 24H, P(C_6H_{11})$_3$), 1.79 (m, 6H, P(C_6H_{11})$_3$), 1.57 (pseudo-q, 12H, P(C_6H_{11})$_3$), 1.28 (m, 18H, P(C_6H_{11})$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 279.55 (m, Os*C*CH$_3$), 42.26 (s, OsC*C*H$_3$), 33.70 (virtual t, $^1J_{PC}$ = 12 Hz, P(C_6H_{11})$_3$), 30.65 (s, P(C_6H_{11})$_3$), 28.20 (virtual t, $^2J_{PC}$ = 6 Hz, P(C_6H_{11})$_3$), 26.51 (s, P(C_6H_{11})$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2): 43.49 (s). ^{19}F NMR (CD_2Cl_2): −79.41 (s). Anal. Calcd for $C_{39}H_{69}Cl_2F_3O_3P_2SOs$: C, 46.93; H, 6.97. Found: C, 46.76; H, 6.90.

Method B (NMR scale). Compound **4** (8.6 mg, 0.010 mmol) was dissolved in CD_2Cl_2 (0.8 mL) and cooled to −35 °C. Methyl trifluoromethanesulfonate (1.2 μL, 0.011 mmol) was added to the dichloromethane solution, and the mixture was stirred at 30 °C. Reaction progress was monitored by ^{1}H and ^{31}P NMR spectroscopy. After 2.5 h, a ^{31}P NMR spectrum showed the following. ^{31}P(121.5 MHz, CD_2Cl_2): δ 43.4 (**10**, 90.2%) and 36.0 (unassigned, 9.8%). Complete conversion to the product was observed after stirring for 20.5 h.

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[Os(≡CMe)(PCy$_3$)$_2$Cl$_3$] (12). The crude residue from the preparation of **11** (0.347 g, 0.409 mmol) was suspended in tetrahydrofuran (100 mL). Tricyclohexylphosphine (0.390 g, 1.39 mmol, 3.40 equiv) was added to the tetrahydrofuran solution. The mixture was refluxed for 1.2 h and then cooled to room temperature. The solvent was removed under vacuum, leaving a pale yellow residue, which was slurried in pentane (25 mL) and diethyl ether (10 mL), stirred for 10 min, and then filtered. The resulting yellow powder was washed with pentane (2 × 5 mL), followed by diethyl ether (3 × 5 mL), and was then dried under vacuum. Crude **12** was dissolved in minimal dichloromethane and placed in the freezer at −35 °C overnight to afford a yellow microcrystalline solid, which was filtered and washed with cold dichloromethane (2 × 3 mL). Two more crops were collected in a similar manner, resulting in 0.232 g (0.262 mmol, 64.1%) of yellow **12**. Pure **12** was obtained after crystallizing crude **12** twice from minimal dichloromethane at −35 °C. ^{1}H NMR (CD_2Cl_2): δ 2.80 (m, 6H, P(C_6H_{11})$_3$), 2.11 (pseudo-d, 12H, P(C_6H_{11})$_3$), 1.84 (m, 24H, P(C_6H_{11})$_3$), 1.56 (m, 6H, P(C_6H_{11})$_3$), 1.56 (t, $^4J_{PH}$ = 2 Hz, OsCCH_3), 1.28 (m, 18H, P(C_6H_{11})$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 274.98 (t, $^2J_{PC}$ = 12 Hz, Os*C*CH$_3$), 42.38 (s, Os*C*CH$_3$), 34.81 (virtual t, $^1J_{PC}$ = 11 Hz, P(C_6H_{11})$_3$), 29.52 (s, P(C_6H_{11})$_3$), 28.52 (virtual t, $^2J_{PC}$ = 5 Hz, P(C_6H_{11})$_3$), 26.99 (s, P(C_6H_{11})$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −10.24 (s). Anal. Calcd for $C_{38}H_{69}Cl_3P_2Os$: C, 51.60; H, 7.86. Found: C, 51.55; H, 7.83.

[Os(=CCH$_2$)(PCy$_3$)$_2$Cl$_2$] (13). Compound **12** (0.243 g, 0.274 mmol) was partially dissolved in tetrahydrofuran (28 mL). Separately, lithium *tert*-butoxide (25 mg, 0.31 mmol, 1.1 equiv) was partially dissolved in tetrahydrofuran (5 mL). The lithium *tert*-butoxide solution was added by pipet to the stirred flask containing **12**. The mixture slowly turned burgundy and was stirred for 2 min, at which time benzene (10 mL) was added. The resulting reaction mixture was stirred for 30 min at 30 °C and filtered, and then the solvent was removed under reduced pressure. The crude residue was filtered through Celite with toluene until the filtrate was colorless, and then the solvent was removed from the combined filtrate and washings under vacuum. The residue was triturated with pentane (10 mL) and then dissolved in minimal dichloromethane, layered with an equal volume of diethyl ether, and placed in the freezer at −35 °C overnight. The reddish-brown crystals were filtered on a cold frit, washed with cold dichloromethane (3 × 4 mL), and then dried *in vacuo*. Another crop was collected in a similar manner, yielding **13** (137 mg, 0.162 mmol, 58.9%). ^{1}H NMR (CD_2Cl_2): δ 2.83 (m, 6H, P(C_6H_{11})$_3$), 2.07 (pseudo-d, 12H, P(C_6H_{11})$_3$), 1.80−1.57 (m, 30H, P(C_6H_{11})$_3$), 1.24 (m, 18H, P(C_6H_{11})$_3$), 0.65 (vt, J_{app} = 2 Hz, 2H, CCH_2). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 274.56 (vt, $^2J_{PC}$ = 9 Hz, Os*C*CH$_2$), 90.36 (m, Os*C*CH$_2$), 34.06 (pseudo-t, J_{app} = 11 Hz, P(C_6H_{11})$_3$), 30.41 (s, P(C_6H_{11})$_3$), 28.46 (pseudo-t, J_{app} = 5 Hz, P(C_6H_{11})$_3$), 27.18 (s, P(C_6H_{11})$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2): 2.56 (s). Anal. Calcd for $C_{38}H_{68}Cl_2P_2Os$: C, 53.82; H, 8.08. Found: C, 53.57; H, 8.47.

[Ru(≡CMe)(PCy$_3$)$_2$Cl$_2$][OTf] (14). Methyl trifluoromethanesulfonate (16.2 μL, 0.143 mmol, 1.00 equiv) was added by syringe to a thawing dichloromethane (9 mL) solution of **1** (107 mg, 0.142 mmol). The mixture was stirred at 30 °C and slowly turned orange. After 5 h, an aliquot was removed and was analyzed by ^{31}P NMR spectroscopy. The spectrum showed a new peak at 53.6 ppm (85%) and starting material at 38.9 ppm (15%). The reaction mixture was stirred overnight at 30 °C, which resulted in a dark orange solution. ^{31}P NMR spectrum showed a peak at 53.6 ppm (**14**, 74%) and a peak at 28.9 ppm ([HPCy$_3$]$^+$, 26%). The mixture was filtered, and the dichloromethane was removed from the filtrate under reduced pressure. The resulting residue was dissolved in minimal dichloromethane, layered with pentane, and cooled to −35 °C. The resulting mixture of orange-brown crystals and colorless needles was filtered on a cold frit and washed four times with 5 mL of a cold dichloromethane/pentane mixture (1:6) followed by cold diethyl ether (5 mL). The crystals were separated by hand for NMR analysis. The colorless crystals were identified as [HPCy$_3$]$^+$, and the orange-brown crystals were identified as crude **14**. ^{1}H NMR (CD_2Cl_2): δ 3.17 (virtual t, 3H, CH_3), 2.87 (m, 6H, P(C_6H_{11})$_3$), 1.79 (m, P(C_6H_{11})$_3$), 1.60 (pseudo-q, P(C_6H_{11})$_3$), 1.32 (m, P(C_6H_{11})$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ not observed (m, Ru*C*CH$_3$), 46.47 (s, RuC*C*H$_3$), 34.30 (virtual t, $^1J_{PC}$ = 10 Hz, P(C_6H_{11})$_3$), 30.88 (s, P(C_6H_{11})$_3$), 28.15 (virtual t, $^2J_{PC}$ = 5 Hz, P(C_6H_{11})$_3$), 26.48 (s, P(C_6H_{11})$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2): 53.56 (s). ^{19}F NMR (CD_2Cl_2): δ −79.30 (s).

[Os(≡CCH$_2$Ph)(PCy$_3$)$_2$Cl$_2$][BF$_4$] (15). Tropylium tetrafluoroborate (64 mg, 0.36 mmol, 1.9 equiv) was added to a stirred solution of compound **4** (0.160 g, 0.192 mmol) in dichloromethane (10 mL). The mixture was stirred for 4 h, and the solvent was removed under vacuum. The residue was suspended in 10 mL of dichloromethane and filtered through Celite. The solvent was removed under vacuum, and the residue was suspended in pentane (10 mL), filtered, washed with pentane (10 mL), washed with diethyl ether (5 × 3 mL), washed with cold tetrahydrofuran (3 × 1 mL), and then dried *in vacuo*, affording crude **15** (0.122 g, 0.121 mmol, 63.2%) contaminated with a small quantity of tropylium tetrafluoroborate (0.06 $C_7H_7BF_4$/**15** by ^{1}H NMR integration). ^{1}H NMR (CD_2Cl_2): δ 7.41 (m, 3H, Ph), 7.12 (d, 2H, Ph), 3.83 (br s, 2H, OsCCH_2Ph), 3.01 (m, 6H, P(C_6H_{11})$_3$), 1.90−1.75 (m, 30H, P(C_6H_{11})$_3$), 1.48 (pseudo-q, 12H, P(C_6H_{11})$_3$), 1.23 (m, 18H, P(C_6H_{11})$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 277.21 (m, Os*C*CH$_2$Ph), 130.34 (s, Ph), 129.74 (s, Ph), 129.21 (s, Ph), 127.57 (s, Ph), 59.46 (s, Os*C*H$_2$Ph), 33.60 (virtual t, $^1J_{PC}$ = 12 Hz, P(C_6H_{11})$_3$), 30.58 (s, P(C_6H_{11})$_3$), 28.18 (virtual t, $^2J_{PC}$ = 6 Hz, P(C_6H_{11})$_3$), 26.48 (s, P(C_6H_{11})$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 44.03 (s).

[Ru(≡CCH$_2$Ph)(PCy$_3$)$_2$Cl$_2$][BF$_4$] (16). Tropylium tetrafluoroborate (23 mg, 0.13 mmol, 0.94 equiv) was added to a stirred dichloromethane (8 mL) solution of Ru(≡C)(PCy$_3$)$_2$Cl$_2$ (101 mg, 0.136 mmol) at 30 °C. The mixture turned dark orange within 1 min and was stirred for 19 h. The reaction mixture was filtered, and the solvent was removed from the filtrate under reduced pressure. The resulting dark residue was suspended in pentane (10 mL), filtered, washed with pentane (10 mL), and then washed with additional pentane (3 × 5 mL). The dark solid was washed with diethyl ether (3 × 5 mL) and then washed with toluene (4 × 5 mL). The resulting yellow powder was dried *in vacuo*, yielding crude [Ru(≡CCH$_2$Ph)(PCy$_3$)$_2$Cl$_2$][BF$_4$] (42 mg, 0.13 mmol, 35%). The ^{31}P NMR spectrum showed one peak at 55.5 ppm. The crude product was recrystallized by vapor diffusion of pentane into a concentrated dichloromethane solution at 30 °C overnight. The filtrate was decanted from the yellow and orange crystals, which were then rinsed three times with 2 mL of the surrounding vapor diffusion solvent and then dried *in vacuo*. The crystals were separated by hand for NMR analysis. The orange crystals were identified as crude **16**, and the yellow-tinted crystals were identified as crude [HPCy$_3$]$^+$. ^{1}H NMR (CD_2Cl_2): δ 7.44 (m, 3H, Ph), 7.19 (m, 2H, Ph), 4.66 (br s, 2H, RuCCH$_2$Ph), 2.87 (m, 6H, P(C_6H_{11})$_3$), 1.90−1.75 (m, P(C_6H_{11})$_3$), 1.50 (pseudo-q, P(C_6H_{11})$_3$), 1.26 (m, P(C_6H_{11})$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 312.00 (m, Ru*C*CH$_2$Ph), 130.57 (s, Ph), 130.28 (s, Ph), 129.65 (s, Ph), 127.60 (s, Ph), 63.27 (s, RuC*C*H$_2$Ph), 34.20 (virtual t, $^1J_{PC}$ = 10 Hz, P(C_6H_{11})$_3$), 30.79 (s, P(C_6H_{11})$_3$), 28.12 (virtual t, $^2J_{PC}$ = 6 Hz, P(C_6H_{11})$_3$), 26.44 (s, P(C_6H_{11})$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 55.38 (s). ^{19}F NMR (CD_2Cl_2): δ −153.27 (br s).

[Os(≡CC(O)Ph)(PCy$_3$)$_2$Cl$_3$] (17). Benzoyl chloride (16.6 μL, 0.144 mmol, 1.20 equiv) was added by syringe to a stirred dichloromethane (13 mL) solution of **4** (100 mg, 0.120 mmol). The yellow solution was stirred overnight at 30 °C for 18.5 h, yielding an orange solution. ^{31}P NMR spectroscopy showed partial conversion of the starting material (23.35 ppm, 21%) to the desired product (−7.85 ppm, 79%). Benzoyl chloride (33.2 μL, 0.288 mmol, 2.40 equiv) was added to the reaction mixture, which was stirred

overnight for 20 h. A ^{31}P NMR spectrum of the orange solution showed only the desired product. The solvent was removed under vacuum, leaving a yellow powder, which was suspended and stirred in pentane (6 mL) for 2 h, filtered, washed with pentane (5 × 4 mL), and then dried *in vacuo*, affording analytically pure **17** (103 mg, 0.106 mmol, 88.0%). ^{1}H NMR (CD_2Cl_2): δ 8.31 (d, $^3J_{HH}$ = 7 Hz, 2H, Ph), 7.71 (t, $^3J_{HH}$ = 7 Hz, 1H, Ph), 7.57 (t, $^3J_{HH}$ = 8 Hz, 2H, Ph), 2.75 (m, 6H, P(C_6H_{11})$_3$), 2.08 (m, 12H, P(C_6H_{11})$_3$), 1.83−1.62 (m, 30H, P(C_6H_{11})$_3$), 1.29−1.07 (m, 18H, P(C_6H_{11})$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 255.33 (vt, $^2J_{PC}$ = 11 Hz; Os*C*C(O)Ph), 192.3 (s, Os*C*C(O)Ph), 136.50 (s, Ph), 133.72 (s, Ph), 131.40 (s, Ph), 129.77 (s, Ph), 36.32 (pseudo-t, J_{app} = 11 Hz, P(C_6H_{11})$_3$), 29.50 (s, P(C_6H_{11})$_3$), 28.34 (pseudo-t, $^2J_{PC}$ = 5 Hz, P(C_6H_{11})$_3$), 26.90 (s, P(C_6H_{11})$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −7.90 (s). Anal. Cacld for $C_{44}H_{71}Cl_3OP_2Os$: C, 54.23; H, 7.34. Found: C, 54.08; H, 7.21.

[Os(≡CH)(PCy$_3$)$_2$Cl$_2$][OTf] (18). Compound **4** (34 mg, 0.041 mmol) was dissolved in toluene (2 mL) and cooled to −35 °C. Trifluoromethanesulfonic acid (3.7 μL, 0.042 mmol, 1.0 equiv) was added to the stirred solution of Os(≡C)(PCy$_3$)$_2$Cl$_2$. After 10 min, the suspension was filtered and the pale tan colored solid was washed with toluene (2 × 2 mL) and pentane (2 × 2 mL). The resulting solid was dried under vacuum, yielding **18** (30 mg, 0.030 mmol, 77%). ^{1}H NMR (CD_2Cl_2): δ 11.02 (s, 1H, Os*CH*), 2.90 (m, 6H, P(C_6H_{11})$_3$), 1.94 (m, 24H, P(C_6H_{11})$_3$), 1.78 (m, 6H, P(C_6H_{11})$_3$), 1.55 (pseudo-q, 12H, P(C_6H_{11})$_3$), 1.28 (m, 18H, P(C_6H_{11})$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2) at −19 °C: δ 285.66 (s, OsCH), 31.71 (pseudo-t, J_{app} = 12 Hz, P(C_6H_{11})$_3$), 30.09 (s, *m*-C of P(C_6H_{11})$_3$), 28.00 (pseudo-t, J_{app} = 6 Hz, P(C_6H_{11})$_3$), 26.39 (s, P(C_6H_{11})$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2): 50.55 (s). ^{19}F NMR (CD_2Cl_2): −79.34 (s). Anal. Calcd for $C_{38}H_{67}Cl_2F_3O_3P_2SOs$: C, 46.38; H, 6.86. Found: C, 45.67; H, 6.40.

[Os(CS)(PCy$_3$)$_2$I$_2$] (20-S). Method A. Green, microcrystalline **4-S** (301 mg, 0.348 mmol) was dissolved in 30 mL of tetrayhydrofuran in a 100 mL round-bottom covered with foil. Sodium iodide (523 mg, 3.49 mmol, 10.0 equiv) was added, and the mixture was stirred 24 h at 30 °C. A ^{31}P NMR spectrum of the reaction mixture showed one resonance corresponding to **20-S** at δ 12.16. The solvent was removed, and the green residue was filtered through Celite with toluene. The Celite was washed with toluene until the filtrate was colorless. The toluene was removed, and the green residue was suspended in 20 mL of pentane, filtered, washed with pentane (2 × 5 mL), and dried *in vacuo*, yielding crude **20-S** (308 mg, 0.294 mmol, 84.6%). Elementally pure material was obtained by recrystallizing crude **20-S** twice from minimal dichloromethane at −35 °C. ^{1}H NMR (CD_2Cl_2): δ 3.54 (m, 6H, P(C_6H_{11})$_3$), 2.08 (pseudo-d, 12H, P(C_6H_{11})$_3$), 1.81 (pseudo-d, 12H, P(C_6H_{11})$_3$), 1.73 (pseudo-d, 6H, P(C_6H_{11})$_3$), 1.52 (pseudo-q, 12H, P(C_6H_{11})$_3$), 1.30 (m, 18H, P(C_6H_{11})$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 241.06 (vt, $^2J_{PC}$ = 7 Hz; CS), 37.0 (pseudo-t, J_{app} = 13 Hz, P(C_6H_{11})$_3$), 31.32 (s, P(C_6H_{11})$_3$), 28.21 (pseudo-t, J_{app} = 5 Hz, P(C_6H_{11})$_3$), 27.07 (s, P(C_6H_{11})$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 11.80 (s). Anal. Cacld for $C_{37}H_{66}I_2P_2OsS$: C, 42.36; H, 6.34. Found: C, 42.04; H, 6.39.

Method B. A pressure vessel was charged with the crude residue from a preparation of **5** (796 mg, 0.729 mmol), tricyclohexylphosphine (650 mg, 2.32 mmol, 3.18 equiv), and 50 mL of tetrahydrofuran, respectively in that order. The mixture was heated to 60 °C for 1.5 h, which resulted in a brown solution. The reaction vessel was wrapped with foil, charged with sodium iodide (932 mg, 6.22 mmol, 8.53 equiv), and stirred for 21.5 h. The solvent was removed, and the green residue was dissolved in toluene (70 mL) and filtered through Celite. The Celite was washed with toluene until the filtrate was colorless. The solvent was removed, and the green residue was suspended in pentane (25 mL), stirred for 10 min, filtered, washed with pentane (2 × 10 mL), washed with diethyl ether (3 × 7 mL), and dried *in vacuo*, yielding crude **20-S** (552 mg, 0.525 mmol, 72.1%). Crude **20-S** can be recrystallized as described in method A.

[Os(≡C)(PCy$_3$)$_2$I$_2$] (20). A pressure vessel was charged with **4** (209 mg, 0.251 mmol) dissolved in toluene (14 mL). Iodotrimethylsilane (360 μL, 2.5 mmol, 10 equiv) was added to the vessel, which was then sealed under nitrogen. The stirred reaction mixture was heated to 120 °C for 10 h, which resulted in a dark orange solution. The solvent was removed, and the residue was suspended in pentane (7 mL), filtered, washed with pentane (3 mL), washed with diethyl ether (2 mL), and then dried *in vacuo*, yielding brown powder containing crude **20** (159 mg, 0.157 mmol, 62.4%). The brown powder was dissolved in minimal dichloromethane and placed in the freezer at −35 °C overnight. The resulting orange crystals were filtered, washed with cold dichloromethane (2 × 4 mL), and dried *in vacuo*. A second crop was obtained in a similar manner, yielding analytically pure **20** (70 mg, 0.069 mmol, 28%). ^{1}H NMR (CD_2Cl_2): δ 3.24 (m, 6H, P(C_6H_{11})$_3$), 2.22 (pseudo-d, 12H, P(C_6H_{11})$_3$), 1.83 (pseudo-d, 12H, P(C_6H_{11})$_3$), 1.71 (pseudo-d, 6H, P(C_6H_{11})$_3$), 1.55 (pseudo-q, 12H, P(C_6H_{11})$_3$), 1.26 (m, 18H, P(C_6H_{11})$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 446.14 (s, Os(C)), 34.71 (pseudo-t, J_{app} = 13 Hz, P(C_6H_{11})$_3$), 31.42 (s, P(C_6H_{11})$_3$), 28.61 (pseudo-t, J_{zpp} = 5 Hz, P(C_6H_{11})$_3$), 27.47 (s, P(C_6H_{11})$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 16.70 (s). Anal. Cacld for $C_{37}H_{66}I_2P_2Os$: C, 43.70; H, 6.54. Found: C, 43.70; H, 6.64.

Control reaction of PCy$_3$ with HOTf. Trifluoromethanesulfonic acid (7.0 μL, 0.079 mmol, 1.0 equiv) was added to a stirred CD_2Cl_2 (0.7 mL) solution of tricyclohexylphosphine (22 mg, 0.077 mmol) at 30 °C. The mixture was stirred for 27 min, yielding [HPCy$_3$][OTf]. ^{1}H NMR (CD_2Cl_2): δ 5.78 (dq, $^1J_{HP}$ = 466 Hz, $^3J_{HH}$ = 4 Hz, 1 H, *H*P(C_6H_{11})$_3$), 2.49 (m, 3H, P(C_6H_{11})$_3$), 2.00 (m, P(C_6H_{11})$_3$), 1.93 (m, P(C_6H_{11})$_3$), 1.79 (m, P(C_6H_{11})$_3$), 1.57 (m, P(C_6H_{11})$_3$), 1.47−1.26 (m, P(C_6H_{11})$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 29.5 (s). ^{19}F NMR (CD_2Cl_2): δ −79.3 (s).

Decomposition of [Os(≡CH)(PCy$_3$)$_2$Cl$_2$][OTf] (18) with an Internal Standard. Compound **18** (7.1 mg, 0.0072 mmol) was dissolved in CD_2Cl_2 (0.7 mL) and placed in a J. Young NMR tube at 30 °C with an insert containing P(OCH_3)$_3$ diluted in C_6D_6. The sample was analyzed by ^{1}H and ^{31}P NMR spectroscopy, and the resonances were integrated relative to the internal standard set at 6 and 10, respectively. For example, a singlet at 10 ppm that integrates to 5 relative to the internal standard will be described as δ 10 (s, 5). The initial NMR spectrum showed that the sample had decomposed in the solid state while stored at 30 °C under nitrogen. ^{31}P NMR spectroscopy showed resonances at δ 50.48 (s, **18**, 29.14), 46.43 (s, 0.38), 30.44 (s, [HPCy$_3$]$^+$, 1.84), 12.22 (s, 2.68). After 2 h, the ^{31}P NMR spectrum showed resonances at δ 50.48 (s, **18**, 18.02), 46.43 (s, 4.09), 30.44 (s, [HPCy$_3$]$^+$, 6.76), and 12.22 (s, 7.81). The ^{1}H NMR spectrum showed resonances at δ 24.64 (d, J = 32 Hz, 0.04), 22.50 (d, J = 37 Hz, 0.22), 11.06 (s, Os(CH), 0.52), and [HPCy$_3$]$^+$ (0.32). After an additional 2 h, the ^{31}P NMR spectrum showed resonances at δ 50.48 (s, **18**, 9.02), 46.43 (s, 6.75), 30.44 (s, [HPCy$_3$]$^+$, 9.94), and 12.22 (s, 13.56). The ^{1}H NMR spectrum showed resonances at δ 24.64 (d, J = 32 Hz, 0.08), 22.50 (d, J = 37 Hz, 0.31), 11.06 (s, Os(CH), 0.26), and [HPCy$_3$]$^+$ (0.44). After an additional 4 h, the ^{31}P NMR spectrum showed resonances at δ 204.00 (s, 0.72), 50.48 (s, **18**, 2.76), 49.38 (s, 1.23), 46.43 (s, 5.80), 30.44 (s, [HPCy$_3$]$^+$, 10.72), 14.19 (s, 1.35), 12.22 (s, 12.24), and 11.02 (s, 1.13). The ^{1}H NMR spectrum showed resonances at δ 24.64 (d, J = 32 Hz, 0.11), 22.50 (d, J = 37 Hz, 0.37), 11.06 (s, Os(CH), 0.07), and [HPCy$_3$]$^+$ (0.58).

Attempted Reaction of [Os(≡C)(PCy$_3$)$_2$Cl$_2$] (4) with ClC(O)*t*-Bu. Pivaloyl chloride (0.8 μL, 0.007 mmol, 1 equiv) was added by syringe to an NMR tube containing compound **4** (5.2 mg, 0.0062 mmol) dissolved in CD_2Cl_2 (0.7 mL). The NMR tube was inverted several times and stored at room temperature overnight. A ^{31}P NMR spectrum of the yellow solution showed only starting material (δ = 23.2).

Attempted Reaction of [Ru(≡C)(PCy$_3$)$_2$Cl$_2$] (1) with ClC(O)-Ph. Benzoyl chloride (1.5 μL, 0.013 mmol, 1.0 equiv) was added

by syringe to an NMR tube containing compound **1** (9.8 mg, 0.013 mmol) dissolved in CD_2Cl_2 (0.8 mL). The NMR tube was inverted several times and stored at room temperature overnight. A ^{31}P NMR spectrum of the yellow solution showed only starting material ($\delta = 38.7$).

Attempted Reaction of [Ru(≡C)(PCy$_3$)$_2$Cl$_2$] (1) with ClC(O)*t*-Bu. Pivaloyl chloride (1.7 μL, 0.014 mmol, 1.1 equiv) was added by syringe to an NMR tube containing compound **1** (10 mg, 0.013 mmol) dissolved in CD_2Cl_2 (0.8 mL). The NMR tube was inverted several times and stored at room temperature overnight. A ^{31}P NMR spectrum of the yellow solution showed only starting material ($\delta = 38.7$).

Reaction of [Se═Mo(N[*t*-Bu]Ar)$_3$] with [Ta(OSi-*t*-Bu$_3$)$_3$] (7). Compound **7** (20 mg, 0.024 mmol, 1.0 equiv) was dissolved in C_6D_6 (0.7 mL) and added by pipet to a stirred solution of Se═Mo(N[*t*-Bu]Ar)$_3$ (17 mg, 0.024 mmol) dissolved in C_6D_6 (0.7 mL). The solution immediately turned orange and was stirred for 30 min at 30 °C. A ^1H NMR spectrum showed complete conversion to Mo(N[*t*-Bu]Ar)$_3$ and **7-Se**.

Reaction of [S═Mo(N[*t*-Bu]Ar)$_3$] with [Ta(OSi-*t*-Bu$_3$)$_3$] (7). Compound **7** (22 mg, 0.026 mmol, 1.0 equiv) was dissolved in C_6D_6 (0.6 mL) and added by pipet to a stirred solution of S═Mo(N[*t*-Bu]Ar)$_3$ (17 mg, 0.026 mmol) dissolved in C_6D_6 (0.6 mL). The solution immediately turned dark red-orange and was stirred for 30 min at 30 °C. A ^1H NMR spectrum showed complete conversion to Mo(N[*t*-Bu]Ar)$_3$ and **7-S**[27] ($\delta = 1.31$).

Reaction of [Os(CS)(PCy$_3$)$_2$I$_2$] (20-S) with [Ta(OSi-*t*-Bu$_3$)$_3$] (7). Compound **7** (8.4 mg, 0.010 mmol, 1.0 equiv) was dissolved in C_6D_6 (0.4 mL) and added by pipet to a stirred, partially dissolved solution of **20-S** (10 mg, 0.010 mmol) in C_6D_6 (0.6 mL). The mixture slowly turned brown. After 10 min the ^1H NMR spectrum showed a broad peak at 1.66 ppm and a few other *t*-Bu-containing products ($\delta = 1.39, 1.35, 1.31, 1.29$). The mixture was stirred overnight at 30 °C. A ^1H NMR spectrum revealed a sharp peak corresponding to Ta(OSi-*t*-Bu$_3$)$_3$I$_2$ ($\delta = 1.43$), the major product, and several other *t*-Bu-containing products.[52]

Reaction of [Os(≡C)(PCy$_3$)$_2$Cl$_2$] (4) with HBF$_4$. Compound **4** (9.9 mg, 0.012 mmol) was dissolved in CD_2Cl_2 (0.6 mL). A 52 wt % ($d = 1.19$) solution of HBF_4 in diethyl ether (2.0 μL, 0.014 mmol, 1.2 equiv) was added to the stirred solution of **4** by syringe. The solution turned dark brown and was stirred at 30 °C for 45 min. ^{31}P NMR spectroscopy showed five phosphorus resonances at δ 51.32 (51%), 49.27 (16%), 30.08 (23%), 14.08 (4%), and 11.06 (6%). ^1H NMR spectroscopy showed a doublet at δ 24.63 ($J = 32.7$ Hz), a broad singlet at δ 10.41, and $[HPCy_3]^+$ in the ratio 0.38:1.65:1, respectively. The broad singlet at δ 10.41 in the ^1H NMR spectrum and the singlet at δ 51.32 in the ^{31}P NMR spectrum are consistent with $[Os(\equiv CH)(PCy_3)_2Cl_2][BF_4]$. After mixing overnight at 30 °C, the ^{31}P NMR spectrum showed mostly $[HPCy_3]^+$ at δ 30.0 (52%) along with resonances at δ 49.21 (15%), 15.47 (5%), 14.07 (10%), 11.05 (12%), and 9.66 (6%). A ^1H NMR spectrum showed the doublet at δ 24.63 and $[HPCy_3]^+$ in a 0.4:1 ratio.

Reaction of [Os(≡C)(PCy$_3$)$_2$Cl$_2$] (4) with [H(OEt$_2$)$_2$][B(C$_6$F$_5$)$_4$]. Compound **4** (10 mg, 0.013 mmol) and $[H(OEt_2)_2][B(C_6F_5)_4]$ (10 mg, 0.012 mmol, 0.92 equiv) were separately dissolved in CD_2Cl_2 (0.4 mL) and cooled to −35 °C. The $[H(OEt_2)_2][B(C_6F_5)_4]$ solution was slowly added by pipet to the stirred solution of **4**. The reaction mixture was warmed to 30 °C while stirring for 30 min. ^{31}P NMR spectroscopy showed a broad resonance at δ 28.5 (60%) and a singlet at δ 34.5 (26%) as well as multiple smaller signals. ^1H NMR spectroscopy did not show resonances corresponding to the Os analogue of $[Ru(=CHPCy_3)(PCy_3)Cl_2][B(C_6F_5)_4]$. Instead, singlets were observed at δ 21.8, 19.2, 17.5, 12.0, and 9.9. The ^{31}P NMR spectra and ^1H NMR spectra were equally complex after the solution was mixed for an additional 2 h at 30 °C.

X-ray Analysis of 4, 4-S, and 15. Crystals were mounted on a standard Bruker SMART CCD-based X-ray diffractometer equipped with a LT-2 low-temperature device and normal focus Mo-target X-ray tube ($\lambda = 0.71073$ Å) operated at 2000 W power (50 kV, 40 mA). Analysis of the data showed negligible decay during data collection; the data were processed with SADABS and corrected for absorption. The structures were solved and refined with the Bruker SHELXTL (version 6.12) software package. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file.

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Supporting Information Available: Synthesis and characterization data for all new compounds, conditions for their reactions, and crystallographic data for **4**, **4-S**, and **15**. This material is available free of charge via the Internet at http://pubs.acs.org.

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