Communication

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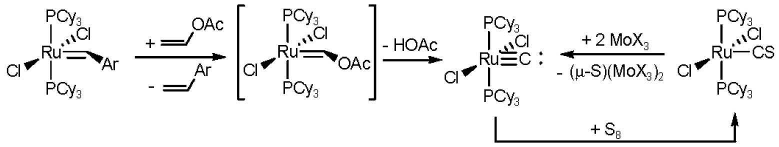

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Two Generalizable Routes to Terminal Carbido Complexes

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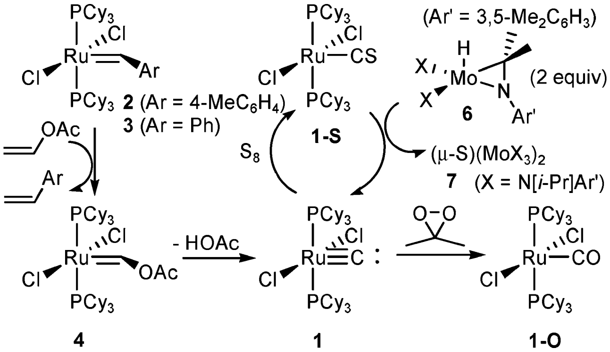
Carbido ligands are of great interest due to their participation in Fischer−Tropsch and related processes for catalytic formation of hydrocarbons and "oxygenates" from synthesis gas.[1−5] Dissociation of CO on the surface of the heterogeneous late metal catalyst to form surface carbide and oxide species is thought to be a critical step in these heterogeneously catalyzed processes,[6,7] which represent a means of converting coal and/or natural gas into gasoline and other liquid fuels. A bridging carbide complex is formed in the decomposition of one Grubbs-type olefin metathesis catalyst.[8] Nevertheless, well-characterized examples of the simplest potential homogeneous model compounds, terminal (one-coordinate) carbido complexes, are very rare.[9−13] Herein we report two newly discovered routes (Scheme 1) to recently reported $[Ru(C)(PCy_3)_2Cl_2]$ (**1**).[10]

Pursuant to synthetic studies aimed at the preparation of Ru complexes containing terminal methylidyne and carbido moieties, we observed that known $[Ru(CH\text{-}p\text{-}C_6H_4Me)(PCy_3)_2Cl_2]$ (**2**)[14] reacted cleanly with 1 equiv of vinyl acetate over the course of 90 min in CH_2Cl_2, affording **1** as a yellow powder in 87% yield upon removal of volatile materials under vacuum, rinsing with pentane, and drying in vacuo. Also identifiable in the ^1H NMR spectrum of the reaction mixture were *p*-methylstyrene and acetic acid. The "parent" complex $[Ru(CHPh)(PCy_3)_2Cl_2]$ (**3**)[14] reacted analogously. Use of excess vinyl acetate (20 equiv) resulted in completion within 30 min, but did not alter the products. At shorter reaction times, resonances consistent with those expected for $[Ru(CHOAc)(PCy_3)Cl_2]$ (**4**) were observable in the ^1H and ^{31}P NMR spectra of the reaction mixtures. In contrast, when **2** was exposed to 20 equiv of vinyl acetate in C_6H_6, **4** was formed cleanly within 15 min, without the formation of detectable quantities of **1**. Decomposition of **4** then took place slowly over the course of several hours, yielding **1** as the major product. Thus, the reaction proceeds via initial metathesis to produce **4**, followed in CH_2Cl_2 by clean elimination of acetic acid in one or more subsequent steps. The good yield of **1** obtained via this method coupled with commercial availability of vinyl acetate and numerous metathesis-active complexes analogous to **2** renders this route exceptionally attractive for the preparation of some carbide complexes. At present, a limitation of this route arises from the formation of acetic acid. Surprisingly, addition of soluble amine bases is counterproductive in that this tends to result in the formation of multiple phosphine-containing products and a reduced yield of **1** (see Supporting Information).

The second new route to **1** is modeled after the CO dissociation step in the Fischer−Tropsch process. Accordingly, the carbonyl and thiocarbonyl complexes, $[Ru(CO)(PCy_3)_2Cl_2]$ (**1-O**) and $[Ru(CS)(PCy_3)_2Cl_2]$ (**1-S**), were investigated as precursors to **1** via chalcogen atom abstraction.

Following unsuccessful attempts with several relatively simple potential atom-abstraction reagents, including PCl_3, PCy_3, $P(OEt)_3$, $Ge(CH[SiMe_3]_2)_2$, 1,3-diisopropylimidazol-2-ylidene, and $V(mes)_3(THF)$ (mes $= 2,4,6\text{-}C_6H_2Me_3$), reactions of **1-O** and **1-S** with $[Mo(N[t\text{-}Bu]Ar)_3]$ (**5**)[15] were examined. Conveniently, Mo−E bond dissociation enthalpy (BDE) values are known for its chalcogenido derivatives $[Mo(E)(N[t\text{-}Bu]Ar)_3]$ (E = O, S: **5-O**, **5-S**).[16] The Mo−O BDE in **5-O** places **5** among the most powerful oxygen atom acceptors reported.[17] However, treatment of **1-O** and **1-S** with 1 or 2 equiv of **5** in THF or C_6D_6 resulted in no reaction, even upon heating to 60 °C for several hours, possibly due to the severe steric demands on a reaction between two such bulky reagents. Accordingly, the smaller "masked" Mo(III) analogue, $[Mo(H)(\eta^2\text{-}Me_2CNAr)(N[i\text{-}Pr]Ar)_2]$ (**6**), reported to be in equilibrium with three-coordinate $[Mo(N[i\text{-}Pr]Ar)_3]$[18] was employed. In this case, 3 equiv of **6** converted **1-S** to **1** smoothly over several hours at 30 °C (Scheme 1), as determined by ^{31}P NMR spectroscopy.

Scheme 1. New Syntheses and Reactions of **1**



Also produced in this reaction was brown $(\mu\text{-}S)[Mo(N[i\text{-}Pr]Ar)_3]_2$ (**7**), which was prepared independently via reaction of $SPPh_3$ with 2 equiv of **6**. Following reaction of **1-S** with **6**, pure **1** was isolated as a yellow powder in 55% yield upon removal of volatile materials under vacuum and subsequent extraction of **7** from the solid mixture using pentane. Exclusion of N_2 from the reaction mixture is advantageous in order to avoid formation of purple $(\mu\text{-}N)[Mo(N[i\text{-}Pr]Ar)_3]_2$ (**8**),[18] which has solubility similar to that of **1** in a variety of solvents and therefore can complicate product separation. In contrast to **1-S**, **1-O** remained unaffected under these conditions. The utility of this atom-abstraction route is underscored in the synthesis of the new carbido complex **9** from $[Ru(CS)(PCy_3)_2(cat)]$ (**9-S**) in 54% isolated yield. To date, we have been unable to prepare **9** from **1** by ligand exchange. We find that **1** is very inert to ligand substitution, which limits its utility in preparing other terminal carbido complexes. Accordingly, we find it necessary to incorporate the desired ancillary ligand set prior to formation of the carbido ligand, as in the synthetic scheme **1-S** → **9-S** → **9** rather than **1** → **9**. Thus, desulfurization of **9-S** is, at present, the only synthetic route to **9**. As thiocarbonyl complexes are not rare,[19,20] desulfurization of a CS ligand is, in principle, a general route to terminal carbides. At present, its major drawback lies in the stoichiometric consumption of **6**, a moderately synthetically challenging and sensitive material. However, formation of **9** demonstrates the utility of this route when the others fail.

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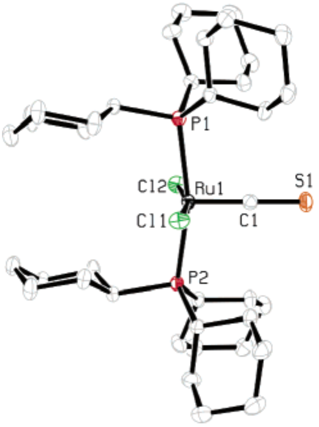

Figure 1. A 50% thermal ellipsoid plot of $[Ru(CS)Cl_2(PCy_3)_2]$ (**1-S**). Selected distances (Å) and angles (°): Ru1−C1, 1.7376(19); Ru1−P1, 2.4211(9); Ru1−P2, 2.4156(9); Ru1−Cl1, 2.3578(7); Ru1−Cl2, 2.3799(7); C1−S1, 1.576(2); Ru1−C1−S1, 179.42(14); P1−Ru1−P2, 165.789(18); Cl1−Ru1−Cl2, 166.290(19); C1−Ru1−Cl1, 97.87(7); C1−Ru1−Cl2, 95.84(7); C1−Ru1−P1, 96.93(6); C1−Ru1−P2, 97.16(6).

Complex **1** is rather unreactive and is stable to air and water. Although its carbido ligand can act as a weak σ-donor to suitable transition metal fragments, this interaction is accompanied by only minor lengthening of the $Ru{\equiv}C$ bond.[9] Reaction of **1** with ethereal HBF_4 yields $[Ru(CHPCy_3)(PCy_3)Cl_2]BF_4$,[21] reported to be a rapidly initiating olefin metathesis catalyst. In related reactions, we find that **1** acts as a chalcogen atom acceptor in some cases. Although **1-O** was not transformed into **1** under the conditions attempted, the reverse transformation was successful. Pyridine-*N*-oxide was unreactive toward **1** under a variety of conditions. Ozone and iodosylbenzene each produced **1-O** in small quantities; the major product was $OPCy_3$. In contrast, addition at ca. −90 °C of 2 equiv of dimethyldioxirane in acetone to a pale yellow solution of **1** in CH_2Cl_2 afforded known **1-O**[22,23] as a yellow−orange powder in 64% isolated yield, following its precipitation and extraction from impurities using acetone.

Having prepared **1** from **1-S**, we investigated the reverse transformation. Accordingly, elemental sulfur converts **1** cleanly into **1-S** in CH_2Cl_2 within 16 h at 30 °C. The conversion appears quantitative by ^1H and ^{31}P NMR spectroscopy, but at longer times, free $SPCy_3$ is produced. Analytically pure **1-S** is thus obtained in 62% yield following filtration to remove excess sulfur, crystallization from the filtered reaction mixture at −35 °C, and recrystallization from THF. Syntheses of **1-S** and **1-O** from **1** are depicted in Scheme 1.

Although **1-S** was formed in good yield from **1**, we found **1-S** most convenient to prepare in two steps from $[RuCl_2(PPh_3)_3]$ by treating crude intermediate complex $[Ru(CS)(OH_2)(PPh_3)_2Cl_2]$[24] with excess PCy_3 without purification.

Dark orange blocks of **1-S** form readily from CH_2Cl_2 at −35 °C; these rapidly revert to a fine yellow−orange powder upon isolation by vacuum filtration. Nevertheless, an X-ray quality crystal so obtained, coated immediately with paratone, and placed in a stream of cold N_2 remained intact and undamaged throughout data collection. The molecule crystallizes in the space group $P\bar{1}$ with a single complex and two CH_2Cl_2 molecules in the asymmetric unit. A thermal ellipsoid plot (50% probability level) is shown (Figure 1). Comparison of the X-ray structures of **1**, **1-O**, and **1-S** reveals very similar square pyramidal cores, with the unique ligand in the apical site. The most important departures are observed in the Ru−C bond lengths, which range from 1.632(6) Å in **1**[9] to 1.705(26) Å in **1-O**,[25] to 1.738(2) Å in **1-S**.

Thus, we have demonstrated that terminal carbido complex **1** is available via two new routes, from differing starting materials. Treatment of **2** or **3** with vinyl acetate affords **1** in 87% isolated yield following olefin metathesis and expulsion of acetic acid; desulfurization of **1-S** using **6** affords **1** in 55% yield. As many carbonyl and thiocarbonyl complexes similar to **1-O** and **1-S** can be obtained straightforwardly from commercial $RuCl_3 \cdot xH_2O$, we are investigating the steric and electronic demands of preparative desulfurization reactions involving these and other reagents, as well as the feasibility of related oxygen atom abstraction from carbonyl complexes, to prepare more reactive terminal carbido complexes. Studies of the scope and mechanism of the metathesis-facilitated conversion of **2** to **1** via **4** are also underway.

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Supporting Information Available: All synthetic procedures; spectroscopic and analytical data for new compounds; tables of crystal data, atomic coordinates, structure solution and refinement, bond lengths and angles, and anisotropic thermal parameters for compound **1-S** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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