Hydrogen Migration and HCl Elimination Promoted by Metal-Centered Nucleophilic Attack on Osmium Hydrido−Carbynes

Greg J. Spivak and Kenneth G. Caulton*

Department of Chemistry, Indiana University, Bloomington, Indiana 47405-4001

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The carbynes $[OsHCl_2(CCH_2R)L_2]$ (R = Ph, CH_3; L = P^iPr_3) react with CO to give, after 1,2-hydride migration from osmium to C_α of the carbyne ligand, the osmium carbene complexes $[OsCl_2(CO)(=CHCH_2R)L_2]$. For R = Ph, reactions with excess CO lead to HCl elimination to form $[OsCl(CO)_2((E)\text{-}CH=CHPh)L_2]$, which reacts with liberated HCl at C_α to yield $[OsCl_2(CO)_2L_2]$ and $CH_2=CHPh$. Abstraction of chloride from either the carbynes or carbenes with $NaBAr'_4$ (Ar′ = 3,5-$C_6H_3(CF_3)_2$) yields the corresponding coordinatively unsaturated carbyne and carbene complexes $[OsHCl(CCH_2R)L_2][BAr'_4]$ and $[OsCl(CO)(=CHCH_2R)L_2][BAr'_4]$, respectively. The carbynes $[OsHCl(CCH_2Ph)L_2]^+$ react with reagent L′ (L′ = CO, HCCR′) to initially give the carbenes $[OsCl(L')(=CHCH_2Ph)L_2]^+$ after 1,2-hydride migration to C_α of the carbyne ligand. These carbenes react further, eliminating HCl and undergoing selective protonation to yield either $[OsCl(CO)_3L_2]^+$ and $CH_2=CHPh$ (with L′ = CO) or the *σ*-vinyl carbyne complexes $[OsCl(CCH_2R')((E)\text{-}CH=CHPh)L_2]^+$ (with L′ = HCCR′).

Introduction

The availability of late transition metal alkylidene complexes which function as olefin metathesis catalysts has allowed their exceptional use in organic synthesis.[1] Although the convenient synthetic utility of such complexes in practical applications continues to expand today, the focus of several recent reports[2] has been the development of new methods of synthesizing late transition metal alkylidene complexes, which have the potential to serve as olefin metathesis catalysts.

One approach toward generating metal−carbene complexes $L_nM(=CRR')$ involves electrophilic addition of $(R')^+$ to nucleophilic carbyne ligands of metal−carbyne complexes $L_nM(CR)$. In fact, a large number of alkylidene complexes have been conveniently prepared by protonating alkylidyne complexes.[3] In many instances, however, it is not clearly understood whether protonation occurs directly at C_α of the carbyne ligand or if the metal is first protonated, followed by rapid hydrogen migration to C_α. Moreover, in at least one case,[3f,k,n] hydrogen migration between the metal and C_α was found to occur quite easily at room temperature.

In a recent preliminary communication[4] regarding the synthesis of the osmium carbynes $[OsHCl_2(CCH_2R)L_2]$, **1** (L = P^iPr_3; R = Ph, **1a**; R = CH_3, **1b**), from the versatile reagent $[OsH_2Cl_2L_2]$ and terminal olefins $CH_2=CHR$, we briefly reported that reactions of **1** with CO at room temperature induce a 1,2-hydride migration from osmium to C_α of the carbyne ligand to yield the corresponding carbenes $[OsCl_2(CO)(=CHCH_2R)L_2]$, **2** (R = Ph, **2a**; R = CH_3, **2b**), as illustrated in eq 1. This novel intramolecular rearrangement offers another approach toward generating osmium alkylidene complexes.[2g−i] We have since expanded upon this unique and interesting chemistry and now report the full details below.

* Corresponding author. E-mail: caulton@indiana.edu.

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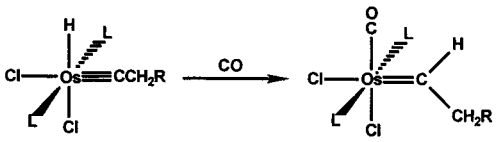

(1)

R = Ph, **2a**
R = CH_3, **2b**

Experimental Section

General Procedures. All manipulations were conducted under an inert atmosphere of prepurified argon using standard Schlenk techniques or in a Vacuum Atmospheres Corp. drybox. All bulk solvents (pentane and CH_2Cl_2) used in large-scale preparations were distilled from appropriate drying agents and stored in bulbs with Teflon taps. All NMR solvents were dried with appropriate drying agents, vacuum distilled, and stored under argon prior to use. NMR spectra (^1H, ^{13}C, and ^{31}P) were obtained on a Varian XL 300 MHz spectrometer, with chemical shifts (in ppm) referenced to residual solvent peaks (^1H and ^{13}C) or external H_3PO_4 (^{31}P). Elemental analyses were performed on a Perkin-Elmer 2400 CHNS/O elemental analyzer in the Department of Chemistry, Indiana University. The complexes $[OsHCl_2(CCH_2R)(P^iPr_3)_2]$ (R = Ph, **1a**; R = CH_3, **1b**)[4] and $NaBAr'_4$[5] were prepared according to the method cited previously.

Reaction of 1a with CO: Formation of $[OsCl_2(CO)(=CHCH_2Ph)(P^iPr_3)_2]$, 2a, and $[OsCl(CO)_2((E)\text{-}CH=CHPh)(P^iPr_3)_2]$, 3. In an NMR tube fitted with a Teflon tap, complex **1a** (0.010 g, 0.016 mmol) was dissolved in CD_2Cl_2 (ca. 0.5 mL) to give a yellow solution. The solution was frozen in liquid nitrogen, and the headspace was evacuated; CO (ca. 1 equiv) was then readmitted into the tube. The solution was thawed and allowed to mix (tumbling) for 2 h to give a pale yellow solution. After such time, all of **1a** had been consumed, and **2a** and **3** were produced in an approximately 1:1 ratio. The spectroscopic (NMR) data for **2a** and **3** were analogous to those cited previously.[6,7]

Synthesis of $[OsCl_2(CO)(=CHCH_2CH_3)(P^iPr_3)_2]$, 2b. A solution of complex **1b** (0.060 g, 0.096 mmol) in CH_2Cl_2 (10 mL) was frozen in liquid nitrogen, and the headspace was evacuated. Excess CO (1 atm) was admitted into the flask, and after thawing, the solution was allowed to stir for 3 h. Filtering the solution through Celite yielded a bright yellow solution. The filtrate was concentrated to ca. 1 mL under reduced pressure and then treated with excess (20 mL) pentane. The murky solution was left in an ice bath for 30 min, and finally the solvent was removed under reduced pressure to yield a slightly pale yellow solid. Yield: 78%. Anal. Calcd for $C_{22}H_{48}Cl_2OOsP_2$: C, 40.55; H, 7.42. Found: C, 40.35; H, 7.28. ^1H NMR (300 MHz, CD_2Cl_2, 20 °C): 1.26 (dvt, N = 14.4 Hz, 18H, PCHCH_3), 1.34 (dvt, N = 13.8 Hz, 18H, PCHCH_3), 2.26 (q, ^3J(HH) = 6.6 Hz, 2H, Os=CHCH_2CH$_3$), 2.76 (m, 6H, PCHCH$_3$), 18.62 (t, ^3J(HH) = 6.6 Hz, 1H, Os=CHCH$_2$-CH$_3$); the methyl resonance of the ethyl group was obscured by the ^{i}Pr proton signals. $^{13}C\{^1H\}$ NMR (75.3 MHz, CD_2Cl_2, 20 °C): 14.97 (s, Os=CHCH$_2$$CH_3$), 19.43 (s, PCH$CH_3$), 20.04 (s, PCH$CH_3$), 25.34 (vt, N = 12.5 Hz, PCHCH$_3$), 55.12 (s, Os=CHCH$_2$CH$_3$), 180.32 (t, ^2J(PC) = 8.3 Hz, Os−CO), 306.41 (br, Os=CHCH$_2$CH$_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2, 20 °C): 12.10 (s, P^iPr$_3$).

Synthesis of $[OsCl_2(CO)_2(P^iPr_3)_2]$, 4. Complex **1a** (0.017 g, 0.028 mmol) in CH_2Cl_2 (2 mL) was frozen in liquid nitrogen, and the contents of the flask were evacuated. Excess CO (1 atm) was admitted into the flask, and upon thawing, the solution was allowed to stir for 48 h. After this time, the remaining excess CO was flushed from the flask with argon, and the yellow solution was once again frozen in liquid nitrogen. After evacuating the flask, excess HCl gas (1 atm) was admitted into the flask. The solution was thawed and allowed to stir for 1.5 h. The volatiles were removed under reduced pressure to yield a yellow powder. Yield: 63%. IR (CD_2Cl_2, cm^{-1}): 2019 (s), 1946 (s). ^1H NMR (300 MHz, CD_2Cl_2, 20 °C): 1.40 (dvt, N = 14.4 Hz, 18H, PCHCH_3), 2.95 (m, 6H, PCHCH_3). $^{13}C\{^1H\}$ NMR (75.3 MHz, CD_2Cl_2, 20 °C): 20.08 (s, PCHCH$_3$), 24.54 (vt, N = 12.3 Hz, PCHCH$_3$), 176.95 (t, ^2J(PC) = 7.3 Hz, Os−CO). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2, 20 °C): 8.03 (s, P^iPr$_3$).

Reaction of 1a with Excess ^{13}CO: Formation of $[OsCl(^{13}CO)_2((E)\text{-}CH=CHPh)(P^iPr_3)_2]$, 3′, and $[OsCl_2(^{13}CO)_2(P^iPr_3)_2]$, 4′. In an NMR tube fitted with a Teflon tap, complex **1a** (0.010 g, 0.016 mmol) was dissolved in CD_2Cl_2 (0.5 mL). The solution was frozen in liquid nitrogen, and the headspace was evacuated. A slight excess of ^{13}CO (ca. 3−4 equiv) was admitted into the NMR tube, and upon thawing, the solution was allowed to mix (tumbling). The NMR (^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$) spectra of the solution were recorded over a 48 h period and revealed the formation of **3′** and **4′**. Complex **3′** was identified by comparison to the literature data.[7] The ^1H NMR data for **4′** were the same as for **4** cited above; $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ data for **4′** follow. $^{13}C\{^1H\}$ NMR (75.3 MHz, CD_2Cl_2, 20 °C): 20.08 (s, PCHCH$_3$), 24.54 (vt, N = 12.3 Hz, PCHCH$_3$), 176.95 (t, ^2J(PC) = 7.3 Hz, Os−CO). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2, 20 °C): 8.02 (t, ^2J(PC) = 7.3 Hz, P^iPr$_3$).

Synthesis of $[OsHCl(CCH_2Ph)(P^iPr_3)_2][BAr'_4]$, 5a. Complex **1a** (0.050 g, 0.082 mmol) in CH_2Cl_2 (10 mL) was treated with 1 equiv (0.082 mmol) of $NaBAr'_4$ (0.072 g). The mixture was stirred for 90 min, and the dark yellow solution was filtered through Celite. The dark yellow filtrate was concentrated to dryness under reduced pressure to yield pure **5a**. Yield: 83%. ^1H NMR (300 MHz, CD_2Cl_2, 20 °C): −9.84 (t, ^2J(PH) = 14.1 Hz, 1H, Os−H), 1.25 (dvt, N = 15.9 Hz, 18H, PCHCH_3), 1.28 (dvt, N = 15.3 Hz, 18H, PCHCH_3), 2.71 (m, 6H, PCHCH$_3$), 3.13 (s, 2H, OsCCH_2Ph), 7.17−7.42 (m, 5H, OsCCH$_2$$Ph$), 7.57, 7.74 (BAr′$_4$). $^{13}C\{^1H\}$ NMR (75.3 MHz, CD_2Cl_2, 20 °C): 19.82 (s, PCHCH$_3$), 20.39 (s, PCHCH$_3$), 26.52 (vt, N = 13.7 Hz, PCHCH$_3$), 57.69 (s, OsCCH$_2$Ph), 129.79, 130.35, 130.77 (all s, Ph), 282.58 (t, ^2J(PC) = 6.1 Hz, OsCCH$_2$-Ph). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2, 20 °C): 62.17 (s, P^iPr$_3$).

Synthesis of $[OsHCl(CCH_2CH_3)(P^iPr_3)_2][BAr'_4]$, 5b. Complex **5b** was prepared as a yellow solid in a manner analogous to that described for **5a**, except the two reagents were allowed to mix for 2.5 h before filtering. Yield: 74%. ^1H NMR (300 MHz, CD_2Cl_2, 20 °C): −9.79 (t, ^2J(PH) = 14.1 Hz, 1H, Os−H), 1.28 (dvt, N = 15.3 Hz, 18H, PCHCH_3), 1.30 (dvt, N = 16.5 Hz, 18H, PCHCH_3), 1.86 (q, ^3J(HH) = 7.5 Hz, 2H, OsCCH_2-CH$_3$), 2.80 (m, 6H, PCHCH$_3$), 7.54−7.71 (BAr′$_4$). $^{13}C\{^1H\}$ NMR (75.3 MHz, CD_2Cl_2, 20 °C): 1.05 (s, OsCCH$_2$$CH_3$), 19.83 (s, PCH$CH_3$), 20.65 (s, PCH$CH_3$), 26.38 (vt, N = 14.1 Hz, PCHCH$_3$), 45.82 (s, OsCCH$_2$CH$_3$), 288.64 (t, ^2J(PC) = 6.9 Hz, OsCCH$_2$CH$_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2, 20 °C): 62.86 (s, P^iPr$_3$).

Formation of $[OsCl(CO)(=CHCH_2Ph)(P^iPr_3)_2][BAr'_4]$, 6a. A crude sample containing an approximately 1:1 mixture of **2a** and **3** (ca. 0.060 g) in CD_2Cl_2 (0.5 mL) was treated with excess $NaBAr'_4$ (ca. 0.09 g, 0.10 mmol) in an NMR tube. After mixing (tumbling) for 1 h, the heterogeneous mixture appeared dark green-yellow. NMR spectroscopy revealed that all of **2a** had been consumed, and the solution now contained an approximately 1:1 mixture of **6a** and **3**. Spectroscopic (NMR) data for **6a** follow. ^1H NMR (300 MHz, CD_2Cl_2, 20 °C): 1.28 (dvt, N = 15.6 Hz, 18H, PCHCH_3), 1.29 (dvt, N = 15.3 Hz, 18H, PCHCH_3), 2.92 (m, 6H, PCHCH$_3$), 3.44 (d, ^3J(HH) = 6.0

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Hz, Os=CHCH_2Ph), 7.72, 7.56 (BAr′$_4$), 17.15 (t, ^3J(HH) = 6.0 Hz, Os=CHCH$_2$Ph). ^{13}C{^{1}H} NMR (75.3 MHz, CD_2Cl_2, 20 °C): 19.31 (s, PCHCH$_3$), 20.05 (s, PCHCH$_3$), 26.12 (vt, N = 13.7 Hz, PCHCH$_3$), 67.62 (s, Os=CHCH$_2$Ph), 128.57, 128.94, 129.94 (all s, Ph), 179.95 (t, ^2J(PC) = 8.7 Hz, Os−CO), 278.82 (t, ^2J(PC) = 7.2 Hz, Os=CHCH$_2$Ph). ^{31}P{^{1}H} NMR (121.4 MHz, CD_2Cl_2, 20 °C: 54.10 (s, P^iPr$_3$).

Synthesis of [OsCl(CO)(=CHCH$_2$CH$_3$)(P^{i}Pr$_3$)$_2$][BAr′$_4$], 6b. Complex **2b** (0.049 g, 0.075 mmol) and 1 equiv of NaBAr′$_4$ (0.066 g, 0.075 mmol) were treated with CH_2Cl_2 (10 mL), and the heterogeneous mixture was stirred for 3 h. The solution was filtered through Celite, and the dark yellow filtrate was concentrated to ca. 1 mL under reduced pressure. Excess pentane (25 mL) was added, and the flask was placed in an ice bath for 30 min. The solvent was then decanted, and the microcrystalline solid that remained was dried under reduced pressure. Yield: 68%. Anal. Calcd for $C_{55}H_{64}BClF_{24}OOsP_2$: C, 43.83; H, 4.10. Found: C, 43.42; H, 4.10. ^{1}H NMR (300 MHz, CD_2Cl_2, 20 °C): 1.28 (dvt, N = 15.0 Hz, 18H, PCHCH_3), 1.30 (dvt, N = 14.7 Hz, 18H, PCHCH_3), 2.18 (q, ^3J(HH) = 5.7 Hz, 2H, Os=CHCH_2CH$_3$), 2.98 (m, 6H, PCHCH$_3$), 7.72, 7.56 (BAr′$_4$), 16.87 (t, ^3J(HH) = 5.7 Hz, 1H, Os=CHCH$_2$CH$_3$). ^{13}C{^{1}H} NMR (75.4 MHz, CD_2Cl_2, 20 °C): 12.45 (s, Os=CHCH$_2$CH_3), 19.01 (s, PCHCH$_3$), 19.90 (s, PCHCH$_3$), 25.80 (vt, N = 13.4 Hz, PCHCH$_3$), 56.22 (s, Os=CHCH$_2$CH$_3$), 178.30 (t, ^2J(PC) = 7.0 Hz, Os−CO), 284.85 (br, Os=CHCH$_2$CH$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, CD_2Cl_2, 20 °C): 53.92 (s, P^iPr$_3$).

Synthesis of [OsCl(CO)$_3$(P^{i}Pr$_3$)$_2$][BAr′$_4$], 7. Complex **5a** (0.020 g, 0.013 mmol) in CH_2Cl_2 (2 mL) was frozen in liquid nitrogen. The flask was evacuated on a gas line manifold, and excess CO (1 atm) was then added. The mixture was warmed to room temperature and allowed to stir for 3 h. The volatiles were then removed under reduced pressure to yield a pale white solid. Yield: 82%. IR (CD_2Cl_2, cm^{-1}): 2131 (w), 2056 (s), 2017 (s). ^{1}H NMR (300 MHz, CD_2Cl_2, 20 °C): 1.43 (dvt, N = 14.7 Hz, 18 H, PCHCH_3), 2.84 (m, 6H, PCHCH$_3$), 7.56, 7.72 (BAr′$_4$). ^{13}C{^{1}H} NMR (75.3 MHz, CD_2Cl_2, 20 °C): 19.81 (s, PCHCH$_3$), 26.53 (vt, N = 13.7 Hz, PCHCH$_3$), 169.20 (tt, ^2J(PC) = 5.9 Hz, ^2J(CC) = 4.1 Hz, Os−CO), 176.98 (dt, ^2J(PC) = 8.3 Hz, ^2J(CC) = 3.6 Hz, Os−CO). ^{31}P{^{1}H} NMR (121.4 MHz, CD_2Cl_2, 20 °C): 17.4 (s, P^iPr$_3$).

Synthesis of [OsCl(*^{13}*CO)$_3$(P^{i}Pr$_3$)$_2$][BAr′$_4$], 7′. In an NMR tube fitted with a Teflon tap, complex **5a** (0.0050 g, 0.0035 mmol) was dissolved in CD_2Cl_2 (0.5 mL). The solution was frozen in liquid nitrogen, and the tube was evacuated. Excess ^{13}CO (1 atm) was admitted into the tube, and after thawing, the solution was allowed to mix (tumbling) for 30 min to yield a colorless solution. Most of the excess ^{13}CO was removed by briefly exposing the solution to a vacuum and then replacing with argon. The reaction was shown to be quantitative by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. The ^{1}H NMR data were the same as those cited for **7**, above; ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR data follow.^{13}C{^{1}H} NMR (75.3 MHz, CD_2Cl_2, 20 °C): 19.81 (s, PCH(CH$_3$)$_2$), 26.53 (vt, N = 13.7 Hz, PCCH$_3$), 169.20 (tt, ^2J(PC) = 5.5 Hz, ^2J(CC) = 4.1 Hz, Os−CO), 176.98 (dt, ^2J(PC) = 8.3 Hz, ^2J(CC) = 3.6 Hz, Os−CO). ^{31}P{^{1}H} NMR (121.4 MHz, CD_2Cl_2, 20 °C): 17.45 (dt, ^2J(PC^1) = 5.5 Hz, ^2J(PC^2) = 8.3 Hz, P^iPr$_3$).

Formation of 6a and 7 from 5a and CO. A CD_2Cl_2 (0.5 mL) solution of **5a** (0.0050 g, 0.0033 mmol) in an NMR tube fitted with a Teflon tap was frozen in liquid nitrogen. The tube was evacuated, and ca. 1 equiv (0.0033 mmol) of CO was added. The mixture was allowed to warm to room temperature and mix (tumbling) for 30 min, after which a pale yellow solution was obtained. NMR spectroscopy (^{1}H and ^{31}P{^{1}H}) revealed the presence of both **7** and **6a** in an approximately 6:1 ratio. The sample was frozen in liquid nitrogen once again and evacuated. Excess (1 atm) of CO was added, and after warming to room temperature and allowing to mix (tumbling) for 30 min, a colorless solution was obtained, which was shown to contain pure **7** by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy.

Synthesis of [OsCl(η^2-HCCSiMe$_3$)(=CHCH$_2$Ph)(P^{i}Pr$_3$)$_2$][BAr′$_4$], 8a. Complex **5a** (0.010 g, 0.0070 mmol) was dissolved in CD_2Cl_2 (0.5 mL) in an NMR tube fitted with a Teflon tap. To this solution, 1 equiv (0.0070 mmol, 1 μL) of HCCSiMe$_3$ was added. The solution was allowed to mix (tumbling) for 24 h, after which it turned pale gray. The reaction was quantitative, as determined by NMR (^{1}H and ^{31}P{^{1}H}) spectroscopy. ^{1}H NMR (300 MHz, CD_2Cl_2, 20 °C): 0.35 (s, 9H, Si(CH_3)$_3$), 1.27 (dvt, N = 15.9 Hz, 18H, PCHCH_3), 1.29 (dvt, N = 15.3 Hz, 18H, PCHCH_3), 1.99 (br m, 2H, Os=CHCH_2Ph), 3.16 (m, 6H, PCHCH$_3$), 7.13−7.40 (m, 5H, Ph), 7.56, 7.72 (BAr′$_4$), 15.91 (br, 1H, Os=CHCH$_2$Ph); the acetylenic hydrogen was partially obscured by the methine hydrogen multiplet. ^{13}C{^{1}H} NMR (75.3 MHz, CD_2Cl_2, 20 °C): 2.07 (s, Si(CH$_3$)$_3$), 19.31 (s, PCHCH$_3$), 20.00 (s, PCHCH$_3$), 24.71 (vt, N = 12.8 Hz, PCHCH$_3$), 68.33 (br, Os(η^2-H$C$$C$SiMe$_3$)), 91.81 (br, Os($\eta^2$-HC$C$SiMe$_3$)), 128.53, 129.20, 130.31 (all s, Ph), 285.06 (t, ^2J(PC) = 8.4 Hz, Os=CHCH$_2$Ph); the CH$_2$Ph carbon was obscured by the solvent peak. ^{31}P{^{1}H} NMR (121.4 MHz, CD_2Cl_2, 20 °C): 45.01 (s, P^iPr$_3$).

Synthesis of [OsCl(η^2-HCC^{t}Bu)(=CHCH$_2$Ph)(P^{i}Pr$_3$)$_2$][BAr′$_4$], 8b. In an NMR tube fitted with a Teflon tap, **5a** (0.010 g, 0.0066 mmol) in CD_2Cl_2 (0.5 mL) was treated with 1 equiv (0.0066 mmol) of HCC^{t}Bu (1 μL). After mixing (tumbling) for 3 h, the solution became pale yellow, almost colorless, and all of the carbyne reagent had been consumed, as determined by NMR (^{1}H and ^{31}P{^{1}H}) spectroscopy. ^{1}H NMR (300 MHz, CD_2Cl_2, 20 °C): 1.26 (dvt, N = 14.7 Hz, 18H, PCHCH_3), 1.28 (dvt, N = 14.7 Hz, 18 H, PCHCH_3), 1.36 (s, 9H, C(CH_3)$_3$), 1.56 (br, 2H, Os=CHCH_2Ph), 3.17 (m, 6H, PCHCH$_3$), 3.26 (br, 1H, HCC^{t}Bu), 7.11−7.37 (m, 5H, Ph), 7.56, 7.72 (BAr′$_4$), 15.02 (br, 1H, Os=CHCH$_2$Ph). ^{31}P{^{1}H} (121.4 MHz, CD_2Cl_2, 20 °C): 41.90 (s, P^iPr$_3$).

Synthesis of [OsCl(CCH$_2$tBu)((*E*)-CH=CHPh)(P^{i}Pr$_3$)$_2$][BAr′$_4$], 9a. An NMR tube was charged with **5a** (0.010 g, 0.0066 mmol) and CD_2Cl_2 (0.5 mL). One equivalent of HCC^{t}Bu (0.0066 mmol, 1 μL) was added, and the solution was allowed to mix (tumbling) for 16 h, at which point it became dark red-purple. NMR spectroscopy revealed complete conversion to **9a**. ^{1}H NMR (300 MHz, CD_2Cl_2, 20 °C): 1.20 (s, 9H, C(CH_3)$_3$), 1.30 (dvt, N = 15.0 Hz, 18H, PCHCH_3), 1.42 (dvt, N = 15.3 Hz, 18H, PCHCH_3), 2.35 (s, 2H, OsCCH_2tBu), 5.90 (d, ^3J(HH) = 12.9 Hz, 1H, OsCH=CHPh), 7.08−7.38 (m, 5H, Ph), 7.47 (d, ^3J(HH) = 12.9 Hz, 1H, OsCH=CHPh), 7.56, 7.72 (BAr′$_4$). ^{13}C{^{1}H} NMR (75.3 MHz, CD_2Cl_2, 20 °C): 19.98 (s, PCHCH$_3$), 20.29 (s, OsCCH$_2$C(CH$_3$)$_3$), 20.53 (s, PCHCH$_3$), 26.48 (vt, N = 13.0 Hz, PCHCH$_3$), 31.23 (s, OsCCH$_2$$CMe_3$), 33.68 (s, OsC$CH_2$-tBu), 125.68, 127.54, 129.29 (all s, OsCH=CHPh), 136.04 (t, ^2J(PC) = 7.6 Hz, OsCH=CHPh), 140.91 (s, OsCH=CHPh), 285.10 (t, ^2J(PC) = 6.2 Hz, OsCCH$_2$tBu). ^{31}P{^{1}H} NMR (121.4 MHz, CD_2Cl_2, 20 °C): 39.54 (s, P^iPr$_3$).

Synthesis of [OsCl(CCH$_2$CH$_3$)((*E*)-CH=CHPh)(P^{i}Pr$_3$)$_2$][BAr′$_4$], 9b. Complex **5a** (0.100 g, 0.0664 mmol) in CH_2Cl_2 (3 mL) was frozen in liquid nitrogen, and the headspace was removed under reduced pressure. Excess propyne (1 atm) was admitted into the flask, and the mixture was allowed to warm to room temperature. After stirring for 20 min, the solution became deep, dark red. The volatiles were removed under reduced pressure, yielding a dark red solid. Yield: 78%. Anal. Calcd for $C_{61}H_{66}BClF_{24}OsP_2$: C, 47.15; H, 4.29. Found: C, 46.55; H, 4.32. ^{1}H NMR (300 MHz, CD_2Cl_2, 20 °C): 1.36 (dvt, N = 13.5 Hz, 18 H, PCHCH_3), 1.39 (dvt, N = 14.7 Hz, 18 H, PCHCH_3), 1.52 (t, ^3J(HH) = 7.8 Hz, 3H, OsCCH$_2$CH_3), 2.45 (q, ^3J(HH) = 7.8 Hz, 2H, OsCCH_2CH$_3$), 3.02 (m, 6H, PCHCH$_3$), 5.97 (d, ^3J(HH) = 12.6 Hz, 1H, OsCH=CHPh), 7.08−7.37 (m, 5H, Ph), 7.50 (d, ^3J(HH) = 12.6 Hz, 1H, OsCH=CHPh), 7.56, 7.72 (BAr′$_4$). ^{13}C{^{1}H} NMR (75.3 MHz, CD_2Cl_2, 20 °C): 8.67 (s, OsCCH$_2$$CH_3$), 19.67 (s, PCH$CH_3$), 20.37 (s, PCH$CH_3$), 25.88 (vt, N = 13.0 Hz, PCHCH$_3$), 46.98 (s, OsCCH$_2$CH$_3$), 126.00, 127.79, 129.65 (all s, Ph), 137.79 (t, ^2J(PC) = 7.6 Hz, OsCH=

CHPh), 142.06 (s, OsCH=*C*HPh), 287.04 (t, ^2J(PC) = 6.1 Hz, Os*C*CH$_2$CH$_3$). ^{31}P{^{1}H} (121.4 MHz, CD_2Cl_2, 20 °C): 44.26 (s, *P*^{i}Pr$_3$).

Reaction of [OsH$_2$Cl$_2$(P^{i}Pr$_3$)$_2$] with CD$_2$=CD(C$_6$D$_5$). The procedure followed was the same as that described[4] for the synthesis of **1a** except the reaction was performed in C_6D_6, rather than C_6H_6. Although the reaction was clean (as determined by ^{31}P{^{1}H} NMR spectroscopy), the ^{1}H NMR spectrum of the product showed (broadened) hydride, benzyl methylene, and ^{i}Pr methyl signals, which presumably came about as a result of H,D exchange with the ^{i}Pr hydrogens catalyzed by the metal.

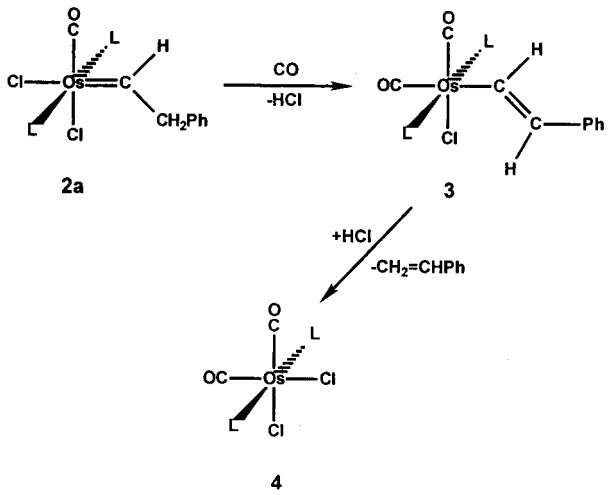
Results and Discussion

Synthesis and Characterization of the Carbenes [OsCl$_2$(CO)(=CHCH$_2$R)(P^{i}Pr$_3$)$_2$], 2. When solutions of **1** are reacted with CO at room temperature, subtle color changes from yellow to pale yellow are observed and the carbenes **2** are produced (eq 1). Thus, when a CD_2Cl_2 solution of **1a** is exposed to approximately 1 equiv of CO, a color change from yellow to lighter yellow is observed after several hours and the known[6] carbene complex **2a** is formed, along with one other additional product (**3**, see below). In contrast to that observed for **2a**, a solution of complex **1b** reacts with *excess* CO over several hours to yield *only* the carbene complex **2b** as a pale yellow solid. Note that in each case hydride migration leads to a formal reduction of the osmium carbyne bond (and, therefore, the osmium formal oxidation state) and that the CO is cis to the resulting carbene ligand (eq 1), consistent with that observed in a recent X-ray structure determination of **2a**.[6] A similar CO-induced hydride migration was also observed in the $IrCo_3$ hydrido−carbyne cluster complex [Cp*Ir(CpCo)$_2$-(μ_2-H)(μ_3-CH)(μ_3-CO)], which yielded the carbene complex [Cp*Ir(CpCo)$_2$(μ_2-CH$_2$)(μ_2-CO)$_2$] upon treatment with CO.[8]

The carbene and CO ligands and the trans arrangement of the phosphine ligands in **2** are easily identified in their NMR spectra. For example, the ^{1}H NMR spectra contain low-field triplets around δ(^{1}H) = 18.7 ppm [^3J(HH) = 6.6 Hz] and two sets of doublets of virtual triplets, consistent with mutually trans phosphines and cis chloride ligands. The CO ligands appear as triplets around δ(^{13}C) = 180 ppm in the ^{13}C{^{1}H} NMR spectra due to coupling to two magnetically equivalent phosphines [^2J(PC) ca. 8 Hz], while those signals attributed to the carbene carbons are observed centered at about δ(^{13}C) = 300 ppm. The substituents on the carbene carbon lie at or near the $OsCl_2$ plane, as revealed by the ^{31}P{^{1}H} NMR spectra of **2**, which show singlets around δ(^{31}P) = 12.0 ppm.

Alternately, if in the synthesis of **2a**, complex **1a** is treated with more than one equivalent of CO, and the progress of the reaction is monitored (via NMR spectroscopy) over time, a number of subsequent reactions are observed beyond the formation of **2a** (Scheme 1), in particular the reductive cleavage of the carbyne ligand from **1a**. Thus, treatment of **1a** with a slight excess of ^{13}CO in CD_2Cl_2 yields after 2 h an approximately 1:1 mixture of ^{13}CO-labeled **2a**, **2a′**, and a second product, the σ-vinyl complex [OsCl(^{13}CO)$_2$((*E*)-CH=CHPh)(L$_2$)], **3′**,

Scheme 1



which is easily identified by comparison of its spectroscopic data with those previously reported.[7] Within an additional 6 h of mixing, **2a′** is completely converted to **3′**, and a third product assigned as [OsCl$_2$(^{13}CO)$_2$L$_2$], **4′**, begins to appear, along with small amounts of styrene. Spectroscopically, the phosphines in **4′** appear as a triplet [^2J(PC) = 8.3 Hz] centered at δ(^{31}P) = 8.0 ppm in the ^{31}P{^{1}H} NMR spectrum, and their trans disposition is clear from the ^{1}H NMR spectrum, which shows a doublet of virtual triplets for the ^{i}Pr methyl groups. Furthermore, the ^{13}CO ligands in **4′** are observed as a triplet at δ(^{13}C) = 176.95 ppm [^2J(PC) = 8.3 Hz], and their cis arrangement is clear from the IR spectrum of unlabeled [OsCl$_2$(CO)$_2$L$_2$], **4**, in CD_2Cl_2, which shows two strong absorptions with frequencies [ν(CO) = 2019, 1946 cm^{-1}] consistent with those observed for other related complexes.[9] As the reaction progresses, the concentrations of **4′** and styrene increase, while that of **3′** decreases; the complete transformation of **3′** into **4′** and styrene is slow, and only about 50% conversion is observed after 48 h.

The transformations leading to the reductive cleavage of the carbyne ligand from **1a** are interesting and warrant further comment. After the addition of one CO ligand to **1a** to produce **2a**, the production of **3** *formally* requires further addition of one CO ligand to **2a** and the elimination of 1 equiv of HCl. The subsequent elimination of styrene to produce **4** is readily explained (at least formally) by selective electrophilic attack of H$^+$ (produced in situ) on the vinyl ligand of **3**, followed by coordination of Cl$^-$ to the osmium center. In fact, **3** is observed to be stable in solution in the absence of excess CO and HCl for at least 48 h. This selectivity toward protonation at C$_\alpha$ of the vinyl ligand is unusual since a number of recent reports[6,10] have established that C$_\beta$ is generally the preferred site of electrophilic attack in osmium vinyl complexes, to yield the corresponding carbene. Furthermore, selective electrophilic attack at C$_\alpha$ of a vinyl ligand (to eliminate olefin) has only been

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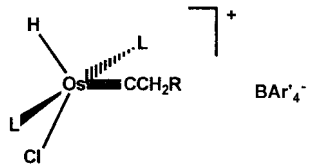
reported in a few cases.[10b,11] Apparently, then, the selectivity toward protonation is quite sensitive to the ligands, and hence the electronic environment, about the osmium. The slow production of **4** from **3** is presumably a function of the low concentration of HCl generated in the reaction. Indeed, treating a CD_2Cl_2 solution of **3** with excess (10 equiv) gaseous HCl cleanly yields **4** within minutes, together with approximately 1 equiv of styrene, as determined by NMR spectroscopy.

The mechanism of eq 1 is of interest due to the 18-electron character of the osmium reagent. We wished to consider that eq 1 begins with chloride loss and therefore sought to effect such removal with electrophiles, in the absence of added CO.

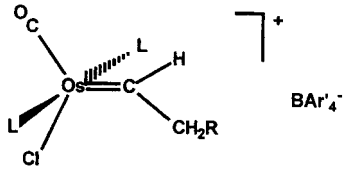
Halide Abstraction from the Carbynes $[OsHCl_2(CCH_2R)(P^iPr_3)_2]$, 1, and the Carbenes $[OsCl_2(CO)(=CHCH_2R)(P^iPr_3)_2]$, 2. Under the proper conditions, a chloride ligand may be abstracted from either complex **1** or **2**. Thus, treatment of the hydrido−carbyne complex **1** with a stoichiometric amount of $NaBAr'_4$ (Ar'_4 = 3,5-$C_6H_3(CF_3)_2$) in CH_2Cl_2 yields, after several hours, the dark yellow, coordinatively unsaturated hydrido−carbyne complexes $[OsHCl(CCH_2R)L_2][BAr'_4]$, **5** (R = Ph, **5a**; R = CH_3, **5b**). The length of time required to



R = Ph, 5a
R = CH_3, 5b

attain completion in these reactions is presumably a function of the low solubility of $NaBAr'_4$ in CH_2Cl_2. In a previous study,[12] it was proposed that the cation of **5a** was formed in equilibrium by the dissociation of a water molecule from $[OsHCl(H_2O)(CCH_2R)L_2]^+$, although it was not described in full detail. Complex **5** is soluble in CH_2Cl_2 and toluene and shows no dramatic differences in the spectroscopic (NMR) signals when compared in each solvent. The most diagnostic features of the $^{13}C\{^1H\}$ NMR spectra of **5** are the signals attributed to the carbyne carbons, which appear as triplets centered at about $\delta(^{13}C)$ = 285 ppm [$^2J(PC)$ = 6.5 Hz] and are shifted slightly downfield relative to the parent carbynes **1**.[4] The trans disposition of the phosphines in **5** is evident from the ^1H NMR spectra, which show doublets of virtual triplets (i.e., diastereotopic inequivalence) for the ^{i}Pr methyl signals. The chemical shifts [$\delta(^1H)$ ca. −9.8 ppm] of the triplets [$^2J(PH)$ = 14 Hz] attributed to the hydride ligands in **5** are shifted only slightly upfield relative to the octahedral complexes **1** [$\delta(^1H)$ ca. −7.0 ppm] and are dramatically different from those reported[13] for the square pyramidal complexes $[OsHCl(CO)L_2]$ (L = tertiary phosphine), in which the hydride [$\delta(^1H)$ ca. −32 ppm] occupies the apical position trans to an empty coordination site. They are, however, similar to those observed for the hydrido−vinylidene complexes $[OsHCl(=C=CHR)L_2]$, in which the H, Cl, and vinylidene ligands adopt a "Y" stereochemistry about the metal.[14] It is therefore anticipated that the stereochemistry about the osmium in **5** is also similar.

Under similar conditions, the golden yellow, coordinatively unsaturated carbene complexes $[OsCl(CO)(=CHCH_2R)L_2][BAr'_4]$, **6** (R = Ph, **6a**; R = CH_3, **6b**), are



R = Ph, 6a
R = CH_3, 6b

isolated from heterogeneous mixtures of the carbene complexes **2** and $NaBAr'_4$ (1:1) in CH_2Cl_2 after several hours. In view of the apparent stability of the cationic, coordinatively *unsaturated* carbyne complexes **5**, it is interesting that even though a vacant coordination site is generated on the metal in the synthesis of **6**, the carbene hydrogen does not migrate back to osmium to regenerate a coordinatively *saturated* (cationic) carbyne complex. One would expect the driving forces of the reaction to be the generation of coordinative saturation about the metal center and the (formal) oxidation of osmium from +4 to +6. We recently determined that the energy of the optimized structure of the transition state for 1,2-hydride migration in $[OsHCl_2(CCH_3)(PH_3)_2]$ to yield $[OsCl_2(=CHCH_3)(PH_3)_2]$ was quite high (ca. 27 kcal/mol),[4] rendering the unimolecular rearrangement energetically not feasible. It is possible that a high transition-state energy also exists between **5** and the corresponding cationic carbynes $[OsHCl(CO)(CCH_2R)L_2]^+$. We find that, in reactions of **5a** with CO, the first *observed* product is the carbene **6a** (see below); clearly, then, adding CO to the metal greatly facilitates (i.e., the thermodynamics and kinetics of) migration of the hydride to C_α in the production of both **2** and **6a**.

Removing the chloride ligand from **2** produces a slight upfield shift in certain ^1H and $^{13}C\{^1H\}$ NMR signals observed for **6**. Thus, the triplet carbene hydrogen signal now appears at about $\delta(^1H)$ = 17.0 ppm [$^3J(HH)$ ca. 6 Hz] in the ^1H NMR spectra, while the $^{13}C\{^1H\}$ NMR spectra show carbene and CO signals centered at about $\delta(^{13}C)$ = 280 ppm [$^2J(PC)$ ca. 7 Hz] and $\delta(^{13}C)$ = 178 ppm [$^2J(PC)$ = 7 Hz], respectively. Doublets of virtual triplets observed for the ^{i}Pr methyl signals in the ^1H NMR spectra are consistent with transoid phosphines about the osmium. In the $^{31}P\{^1H\}$ NMR spectra, singlets are observed around $\delta(^{31}P)$ = 54 ppm, implying that the carbene substituents preferentially occupy the plane that bisects the plane containing the osmium and phosphorus atoms. It is, of course, impossible to know from the NMR data the angles between the π-acceptor (i.e., CO and CCH_2R) and π-donor (i.e., Cl) ligands about the metal in **6**. In view of our interest in establishing the stereochemistry of **6**, we sought an

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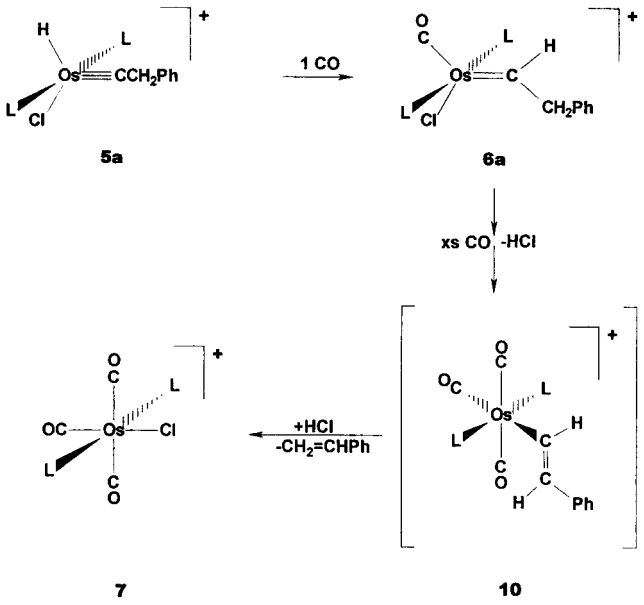
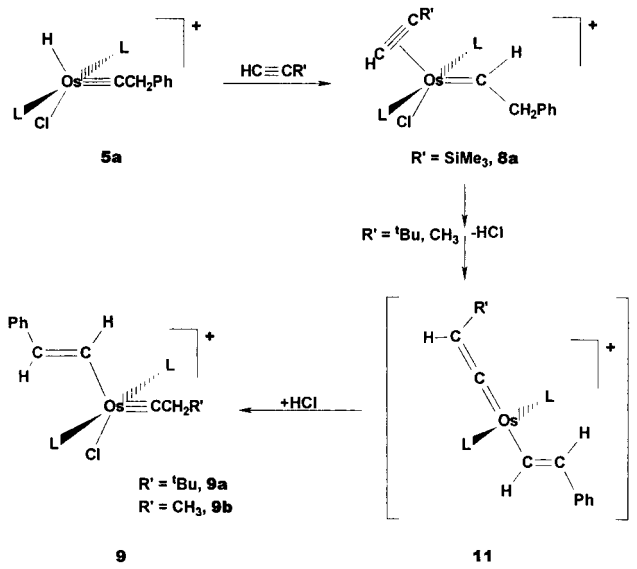
Scheme 2



Scheme 3



X-ray structure determination of **6b**. However, despite numerous attempts at growing X-ray quality single crystals, we were unsuccessful.

Reactivity of [OsHCl(CCH$_2$Ph)(P^{i}Pr$_3$)$_2$][BAr′$_4$], 5a, toward Nucleophiles L′. A facile migration of hydride to C_α was also observed in reactions of CH_2Cl_2 solutions of **5a** with various nucleophiles L′ (L′ = CO, HCCR′) to yield (initially) the corresponding carbene adduct $[OsCl(L')(=CHCH_2Ph)L_2]^+$. However, the course of the reaction beyond the formation of the carbene depends on the nature of L′.

(a) L′ = CO. Treatment of a solution of **5a** with approximately 1 equiv of ^{13}CO produces a color change from dark yellow to pale yellow after 30 min and yields the corresponding ^{13}CO-labeled analogue of the carbene complex **6a** and a second product, the carbonyl complex $[OsCl(^{13}CO)_3L_2]^+$, **7′**, in approximately a 1:6 ratio, along with small amounts of styrene. If this same solution is further treated with excess ^{13}CO (i.e., greater than 1 equiv), or if a solution of **5a** is treated with excess (1 atm) CO, within 30 min the solution becomes nearly colorless and only the tricarbonyl complex is observed, along with 1 equiv of styrene (Scheme 2). Complexes of the type $[OsX(CO)_3(PR_3)_2]^+$ (X = halide; PR_3 = tertiary phosphine) have been prepared previously by other methods.[9c,d] Complex **7′** shows a doublet of triplets centered at $\delta(^{31}P) = 17.4$ ppm [$^2J(PC^1) = 5.5$ Hz and $^2J(PC^2) = 8.3$ Hz, where C^1 corresponds to the CO ligand trans to chloride and C^2 corresponds to those CO ligands trans to one another] in its $^{31}P\{^1H\}$ NMR spectrum and two multiplets in its $^{13}C\{^1H\}$ NMR spectrum for the two sets of CO ligands, a triplet of triplets at $\delta(^{13}C) = 169.2$ ppm [$^2J(PC^1) = 5.5$ Hz, $^2J(CC) = 3.6$ Hz] for the CO ligand trans to chloride, and a doublet of triplets at $\delta(^{13}C) = 177.0$ ppm [$^2J(PC^2) = 8.3$ Hz, $^2J(CC) = 3.6$ Hz] for the two trans CO ligands (see Scheme 2). Further support for the identity of **7′** is found in the IR spectrum of unlabeled $[OsCl(CO)_3(L_2][BAr'_4]$, **7**, in CD_2Cl_2, which reveals three absorptions [$\nu(CO) = 2131, 2056, 2017$ cm^{-1}] with frequencies similar to those observed for analogous complexes.[9c,d] Unfortunately, complex **7** is formed quite rapidly in these reactions, and no intermediates containing vinyl ligands (e.g., **10**, see Scheme 2) could be detected during reactions at 20 °C, although the ruthenium analogue of **10**, $[Ru(CO)_3((E)\text{-}CH{=}CHPh)(P^iPr_3)_2]^+$, has been reported recently.[11] Moreover, our attempts to scavenge any eliminated HCl during the reaction using triethylamine, 2,6-lutidine, DBU, lithium 2,2,6,6-tetramethylpiperide, and even P^iPr_3 were thwarted by the rapid (seconds) formation of the vinylidene complex $[OsHCl(=C{=}CHPh)L_2]$[12] from **5a**; in contrast, poly(4-vinylpyridine) had no effect on the outcome of the reaction with CO. Evidently the methylene hydrogens of the benzyl group of **5a** are acidic and easily deprotonated by even weak bases. Indeed, this is certainly not surprising in view of the fact that **5a** is cationic. Thus, as in Scheme 1, loss, then readdition, of HCl is a central theme.

(b) L′ = HCCR′. When these reactions were extended to terminal acetylenes, a somewhat different reactivity pattern emerged. Thus, in reactions of **5a** with various terminal acetylenes HCCR′ (R′ = $SiMe_3$, ^{t}Bu, Me), in each case, initial η^2-coordination of the acetylene was accompanied by a 1,2-migration of the hydride to C_α to give the corresponding alkyne−carbene adduct $[OsCl(\eta^2\text{-}HCCR')(=CHCH_2Ph)L_2]^+$, **8** (Scheme 3). For example, treatment of **5a** with 1 equiv of $HCCSiMe_3$ in CD_2Cl_2 at room temperature gave, after 24 h, a pale gray solution of the alkyne−carbene complex $[OsCl(\eta^2\text{-}HCCSiMe_3)(=CHCH_2Ph)L_2]^+$, **8a**. The ^1H NMR spectrum of **8a** revealed diastereotopic inequivalent ^{i}Pr methyls (and trans phosphines) and showed the presence of a carbene hydrogen as a broad signal with no resolved coupling at $\delta(^1H) = 15.9$ ppm. This carbene was also evident in the $^{13}C\{^1H\}$ NMR spectrum as a triplet at $\delta(^{13}C) = 285.1$ ppm [$^2J(PC) = 8.4$ Hz], corresponding to the carbene carbon; the acetylenic carbons were observed as weak, slightly broadened signals at $\delta(^{13}C) = 91.8$ ($HCCSiMe_3$) and $\delta(^{13}C) = 68.3$ ($HCCSiMe_3$) ppm, in the region expected for η^2-HCCR ligands acting as two-electron-donor ligands.[15] Attempts to promote any further reaction by heating a solution

(15) Templeton, J. L. *Adv. Organomet. Chem.* **1989**, *29*, 1.

of **8a** at 70 °C for several hours only produced **5a**, $HCCSiMe_3$, and a small amount of unidentified decomposition products.

When terminal acetylenes with other R′ groups were employed, complex **8** formed more rapidly; however, further reactions were observed (Scheme 3). Thus, reaction of **5a** with 1 equiv of HCC^tBu yields a pale yellow, almost colorless solution of $[OsCl(\eta^2\text{-}HCC^tBu)(=CHCH_2Ph)L_2]^+$, **8b**, within 3 h. The NMR (^1H and $^{31}P\{^1H\}$) spectroscopic data for **8b** showed it to be structurally similar to **8a**: (i) a clear indication of trans-disposed phosphines, and (ii) a (broad) carbene hydrogen signal at $\delta(^1H) = 15.0$ ppm. However, allowing the reaction to continue for a further 16 h results in the formation of the reddish-purple σ-vinyl−carbyne complex $[OsCl(CCH_2tBu)((E)\text{-}CH{=}CHPh)L_2]^+$, **9a**. Thus, in this reaction, the original carbyne skeleton has now become a vinyl group! Similarly, when the less bulky acetylene $HCCCH_3$ is used, the reaction proceeds much more rapidly. In fact, when solutions of **5a** are exposed to an excess of $HCCCH_3$, a rapid (less than 1 min) color change from yellow to pale gray is observed, and after 20 min, the deep, dark red complex $[OsCl(CCH_2CH_3)((E)\text{-}CH{=}CHPh)L_2]^+$, **9b**, is formed. Once again, the carbyne is not passive, but has become a vinyl ligand (and not merely a carbene). It is believed that the pale gray intermediate that precedes the formation of **9b** is the (expected) propyne−carbene adduct, $[OsCl(\eta^2\text{-}HCCCH_3)(=CHCH_2Ph)L_2]^+$, **8c** (doublets of virtual triplets are observed for the ^{i}Pr methyl groups, and a broad carbene hydrogen signal is observed at $\delta(^1H) = 15.6$ ppm, in the ^1H NMR spectrum, while a sharp singlet at $\delta(^{31}P) = 43.3$ ppm appears in the $^{31}P\{^1H\}$ NMR spectrum); however, its rapid reaction to yield **9b** precluded its full characterization. The vinyl ligands are easily identified in the ^1H NMR spectra of **9a** and **9b**, which show doublets around $\delta(^1H) = 5.9$ ppm and $\delta(^1H) = 7.5$ ppm, corresponding to H_α and H_β, respectively, with $^3J(HH) = 12.5$ Hz, indicative of a trans coupling. In both cases, the carbyne carbon is observed around $\delta(^{13}C) = 286$ ppm as a triplet [$^2J(PC)$ ca. 6.1 Hz].

It is important to note not only the differences in the rates of formation of complex **8** (R′ = Me > ^{t}Bu > $SiMe_3$) but also that for R′ = $SiMe_3$ complex **8a** does *not* react further to yield $[OsCl(CCH_2SiMe_3)((E)\text{-}CH{=}CHPh)L_2]^+$. Considering the relative bulkiness of the R′ groups examined and the bulkiness of the P^iPr_3 ligands on the osmium, it's reasonable to assume that steric demands play a role in determining both the differences in reaction rate and outcome. Note the thermodynamic implication of this result: the η^2-alkyne−carbene isomer is less stable than the vinyl−carbyne form.

The isomerizations observed in these reactions involve one hydrogen moving from (either carbon of) the carbene of **8b** and **8c** to carbon of the η^2-alkyne. Since HCl elimination is a fundamental step in Schemes 1 and 2, we proceeded with a similar hypothesis. After **5a** adds HCCR′ to yield **8**, we believe the acetylene ligand isomerizes to a vinylidene ligand, accompanied by rapid loss of HCl to give the σ-vinyl−vinylidene intermediate complex $[OsCl(=C{=}CHR')((E)\text{-}CH{=}CHPh)L_2]^+$, **11**. The intermediate **11** then undergoes selective protonation at C_β of the vinylidene ligand and adds Cl^- to give the σ-vinyl−carbyne complex **9**. It is interesting and important that this mechanism suggests C_β of the vinylidene ligand is the preferred site of electrophilic attack over attack at C_α of the vinyl ligand, which is the pattern in Schemes 1 and 2. However, protonating vinylidene ligands to give carbynes is well documented.[16] We attempted to establish the fate of the various hydrogens in **8b** and **8c** by preparing $[OsDCl(CCD_2Ph)L_2]^+$, but were frustrated by hydrogen−deuterium exchange with the ^{i}Pr groups of the phosphine ligands during the attempted synthesis of $OsDCl_2(CCD_2Ph)L_2$.[17]

Concluding Remarks

We have demonstrated in this report an alternate approach to generating osmium alkylidene complexes via nucleophilic attack on osmium hydrido−carbyne precursor complexes, in particular, $[OsHCl_2(CCH_2R)L_2]$ and $[OsHCl(CCH_2R)L_2]^+$. For the former class of complexes, in particular for R = Ph, further reactions were observed beyond the formation of the alkylidene complex in the presence of an excess of the nucleophile (i.e., CO), which lead to complete cleavage of the carbyne ligand from the metal. In reactions of the coordinatively unsaturated complex $[OsHCl(CCH_2R)L_2]^+$ (R = Ph) with L′, alkylidene formation was also observed initially; however the ultimate fate of the reaction was determined by the nature of L′. Thus, for L′ = CO, cleavage of the carbyne ligand from the metal was observed, while for L′ = HCCR′, the alkylidene complexes $[OsCl(\eta^2\text{-}HCCR')(=CHCH_2Ph)L_2]^+$ isomerized to the corresponding σ-vinyl−carbyne complexes $[OsCl(CCH_2R')((E)\text{-}CH{=}CHPh)L_2]^+$.

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