What are the primary products of reactions between anionic hydrides and HC≡CPh?

Letter

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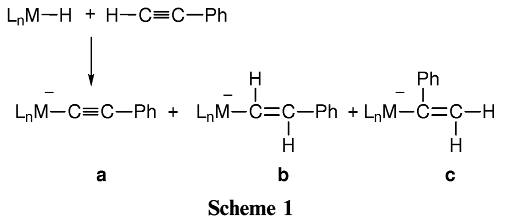
Reactions of phenylacetylene with $[RuH_2(CO)L]^-$ [L is the pincer ligand C_6H_3-2,6-$(CH_2PBu^t_2)_2$], $[RuH_3(CO)(PPr^i_3)_2]^-$ and $[ReH_3(NO)(PPr^i_3)_2]^-$ have afforded the new anionic σ-alkynyl and vinyl complexes *trans*-$[RuH(C{\equiv}CPh)(CO)L]^-$, *cis*-$[RuH_2(C{\equiv}CPh)(CO)(PPr^i_3)_2]^-$, *cis*-$[RuH_2(CPh{=}CH_2)(CO)(PPr^i_3)_2]^-$ and *cis*-$[ReH_2(CPh{=}CH_2)(NO)(PPr^i_3)_2]^-$, all as the $[K(18\text{-crown-}6)]^+$ salts. Formation of the acetylides does not involve unsaturated species and takes place *via* $[M{-}C(Ph){=}CH_2]$ vinyl intermediates.

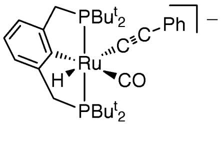
Chemistry of anionic transition metal hydrides has attracted little attention in contrast to the related neutral and cationic species.[1] We decided to investigate the reactivity of *trans*-$[RuH_2(CO)L]^-$ (1)[2a] [L is the pincer ligand C_6H_3-2,6-$(CH_2PBu^t_2)_2$], $[RuH_3(CO)(PPr^i_3)_2]^-$ (2)[2b] and $[ReH_3(NO)(PPr^i_3)_2]^-$ (3)[2b] {all are $[K(18\text{-crown-}6)]^+$ salts} in a typical reaction of metal hydrides—insertion of alkynes into the M—H bond. Three primary organometallic products could be anticipated with HC≡CPh (Scheme 1). Product **a** can be formed by H_2/PhC_2^- replacement after protonation of $[HML_n]^-$ by HC≡CPh.[3] Species **b** and **c** are insertion products with vinyl ligands attached *via* the α or β-carbon atoms, respectively. This communication reports the finding that **c** is the primary product with complexes **1**–**3**.



Scheme 1

A fast NMR tube reaction of *trans*-$[RuH_2(CO)L]^-$ (**1**) and two equivalents of HC≡CPh in pyridine-d_5 cleanly afforded a ruthenium product and one equivalent of $H_2C{=}CHPh$. The product could be isolated from pyridine or THF and characterized as *trans*-$[RuH(CCPh)(CO)L]^-$ (**4**) by ^1H, ^{31}P and ^{13}C NMR, IR spectroscopy and elemental analysis. The *trans*-H—Ru—C≡CPh disposition was confirmed by the difference ^1H NOE (nuclear Overhauser effect) spectra (Fig. 1). The anion **4** is not a very strong base and no protonation was observed with 2–4 equivalents of methanol in THF.

A second anionic complex, $[RuH_3(CO)(PPr^i_3)_2]^-$ (**2**), reacted with phenylacetylene to afford an isolated mixture of two products in a 1 : 2 ratio. The minor product is of the **a** type, *cis*-$[RuH_2(C{\equiv}CPh)(CO)(PPr^i_3)_2]^-$ (**5**), and was identified by NMR and IR spectroscopy. Complexes **4** and **5** have very similar —C≡CPh ^{13}C NMR and IR features (Table 1). The major component of the mixture is the vinyl complex *cis*-$[RuH_2(CPh{=}CH_2)(CO)(PPr^i_3)_2]^-$ (**6**) according to the ^1H and ^{13}C NMR data.



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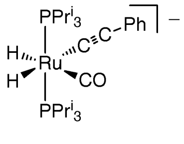

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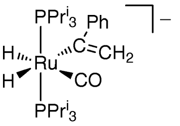

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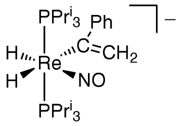

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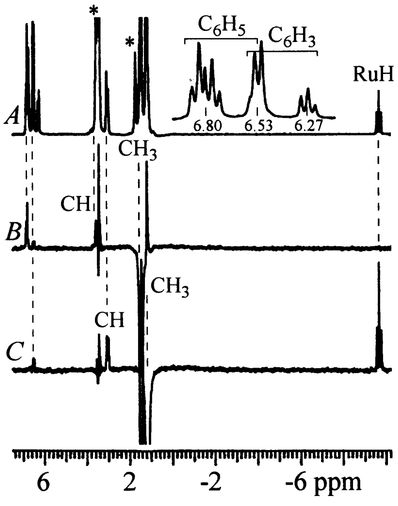
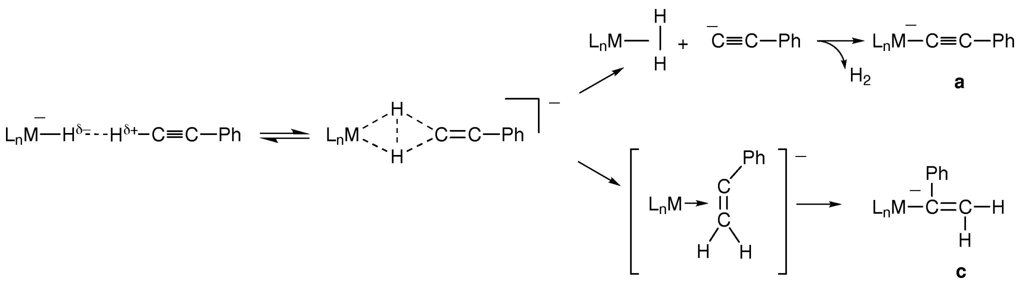


Fig. 1 (*A*) Regular ^1H NMR and (*B*, *C*) difference NOE spectra of the acetylide **4**. The RuH and $—C{\equiv}C—C_6H_5$ fragments are *trans* since their enhancements in *B* and *C* originate from inequivalent CH_3 groups on the opposite sides of the P—C—P plane in **4**. Solvent resonances (THF-d_8) are shown by stars, the one at δ 3.58 is overlapped with the intense line of $[K(18\text{-crown-}6)]^+$.

Table 1 Selected spectroscopic data for complexes **4**–**7**

Complex	δ(M—H)	δ(M—C≡)	δ(≡CPh)	δ(C_{ipso})
4[a]	−9.67	151.59	113.88	134.91
5[b]	−11.10, −8.27	148.24	113.24	135.30
	δ(M—H)	δ(M—CPh)	δ(=CH_2)	δ(C_{ipso})
6	−12.39, −7.52	191.96	121.62	167.82
7	−5.45, −3.78	182.06	120.30	165.75

[a] $\nu_{C\equiv C} = 2065\ cm^{-1}$. [b] $\nu_{C\equiv C} = 2058\ cm^{-1}$.



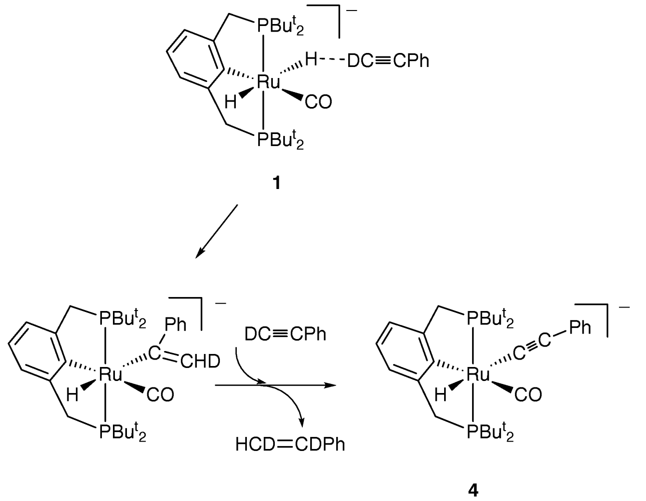
Scheme 2

Finally, when rhenium trihydride, $[ReH_3(NO)(PPr^i_3)_2]^-$ (**3**), was reacted with phenylacetylene, slow and clean formation of *cis*-$[ReH_2(CPh{=}CH_2)(NO)(PPr^i_3)_2]^-$ (**7**) was complete in 6 h. No intermediates could be detected in the reaction solution by ^{31}P NMR. The isolated product was characterized by ^1H, ^{31}P and ^{13}C NMR, IR spectroscopy, and elemental analysis. Facile protonation of **7** cleanly afforded a stable styrene complex, $ReH_2(CH_2{=}CHPh)(NO)(PPr^i_3)_2$, which will be reported elsewhere.

The results of three different reactions of the ruthenium and rhenium complexes allow mechanistic considerations. The interaction that brings together coordinatively saturated, thermally stable hydrides **1**–**3** and an alkyne molecule could be the $M{-}H^{\delta-}\cdots{}^{\delta+}H{-}C$ hydrogen (also termed 'dihydrogen') bonding shown in Scheme 2.[4] The experimental evidence for a reversible formation of the $[L_nM(\mu\text{-}H_2)CCPh]^-$ transient species is represented by the reported H/D scrambling in a $FeH_2(dippe)_2/PhC{\equiv}CD$ system.[5] Scheme 2 shows further feasible rearrangements of $[L_nM(\mu\text{-}H_2)CCPh]^-$, which are either protonation of the metal fragment or hydride transfer to the C_α atom of phenylacetylene. An alternative $C_\beta{-}H$ bond formation (not shown) appears less likely for geometric reasons. In agreement with this, no **b**-type product has been detected in the reactions of complexes **1**–**3**.

The acetylides **4** and **5** apparently do not result from protonation of **1** and **2** by phenylacetylene. For example, complex **4** is not a *primary* organometallic product since it is formed along with styrene. Furthermore, for **4**, the interpretation of Scheme 2 invoking H_2 loss and a 16-electron intermediate is implausible in neat pyridine where the intermediate would afford a pyridine complex.

A deuterium-labeling experiment with **1** and phenylacetylene-d clearly indicated that formation of the acetylide **4** involved a **c**-type primary product. *trans*-$[RuH_2(CO)L]^-$ and two equivalents of $DC{\equiv}CPh$ reacted on mixing in an NMR tube, cleanly affording the monohydride **4** and one equivalent of $HCD{=}CDPh$ (Scheme 3). The deuteriated styrene showed two terminal CH triplets in the ^1H NMR spectrum in a 3.5 : 1 ratio at δ 5.68 ($^3J_{H\text{-}D}$ = 2.7 Hz) and δ 5.12 ($^3J_{H\text{-}D}$ = 1.6 Hz), respectively. Thus, only one hydride took part in the reaction and it was transferred to the C_α atom of phenylacetylene, affording the vinyl intermediate shown in Scheme 3.



Scheme 3

All of the above indicate that generally (*a*) reactions of terminal acetylenes with metal hydrides may not require formation of unsaturated intermediates, (*b*) σ-acetylide complexes may not be intermediate species in hydrogenation of acetylenes, but (*c*) their formation might take place *via* intermediate **c**-type vinyl complexes.

Experimental

All reactions and sample preparations were carried out in dry solvents under purified nitrogen in an Innovative Technology glovebox equipped with a vacuum line and a −35 °C refrigerator. Throughout this paper, the NMR data are reported with the apparent coupling of virtual triplets (vt) denoted as ^vJ.

Preparation of *trans*-$[RuH(C{\equiv}CPh)(CO)\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t_2)_2\}][K(18\text{-crown-}6)]$ (4)

$PhC{\equiv}CH$ (74 mg, 0.72 mmol) was added to a solution of $[RuH_2(CO)\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t_2)_2\}][K(18\text{-crown-}6)]$ (300 mg, 0.36 mmol) in THF (3 mL) or pyridine (1.5 mL). The mixture was stirred for 1 h. Addition of 12 mL of hexane caused the product to crystallize out as a white solid. It was isolated by filtration, washed with 3 × 3 mL of hexane and dried under vacuum. Yield from THF: 278 mg (*ca.* 82%). Yield from pyridine: 316 mg (*ca.* 94%). Anal. calcd for $C_{45}H_{73}KO_7P_2Ru$ (928.195): C, 58.23; H, 7.93. Found: C, 57.83; H, 8.05. IR (Nujol): $\nu_{C\equiv C}$ 2065 cm^{-1}, ν_{CO} 1852 cm^{-1}, ν_{RuH} 1583 cm^{-1}. ^1H NMR (200 MHz, THF-d_8): δ −9.67 (t, $^2J_{H\text{–}P}$ = 21.7 Hz, 1H, Ru*H*), 1.22, 1.50 (vt, $^vJ_{H\text{–}P}$ = 5.6 Hz, 36H, C*H*$_3$), 3.07 (dvt, $^2J_{H\text{–}H}$ = 14.9 Hz, $^vJ_{H\text{–}P}$ = 3.7 Hz, 2H, C*H*$_2$), 3.51 (s, 24H, crown-C*H*$_2$), 3.55 (overlapped with the crown resonance, 2H, C*H*$_2$), 6.31 (m, 1H, C_6H_3), 6.57 (m, 3H, Ar), 6.86 (m, 4H, C_6H_5). $^{31}P\{^1H\}$ NMR (80 MHz, THF-d_8): δ 107.4. $^{13}C\{^1H\}$ NMR (50 MHz, THF-d_8): δ 30.23, 29.88 (vt, $^vJ_{C\text{-}P}$ = 2.2 Hz, *C*H$_3$), 35.55 (vt, $^vJ_{C\text{–}P}$ = 8.1 Hz, P*C*), 37.61 (vt, $^vJ_{C\text{–}P}$ = 3.4 Hz, P*C*), 42.04 (vt, $^vJ_{C\text{–}P}$ = 10.0 Hz, P*C*H$_2$), 71.12 (s, crown-*C*H$_2$), 113.88 (s, ≡*C*Ph), 118.41 (vt, $^vJ_{C\text{–}P}$ = 7.6 Hz, *C*H, Ru—Ar), 120.13 (s, *C*H, Ru—Ar), 120.23, 127.41, 130.68 (s, *C*H, C_6H_5), 134.91 (s, C_{ipso}, C_6H_5), 149.04 (vt, $^vJ_{C\text{–}P}$ = 10.3 Hz, *C*, Ru—Ar), 151.59 (t, $^2J_{C\text{–}P}$ = 10.7 Hz, Ru—*C*≡), 188.57 (t, $^2J_{C\text{–}P}$ = 7.6 Hz, Ru*C*), 212.46 (t, $^2J_{C\text{–}P}$ = 10.1 Hz, *C*O). Assignment of the ^{13}C signals was confirmed by gated-decoupled ^{13}C NMR. Hydride-coupled ^{13}C NMR: the carbonyl and ligand metal-bound carbon atoms both showed small $^2J_{C\text{–}H}$ couplings of 5.2 and *ca.* 5 Hz, respectively. The $-C{\equiv}CPh$ carbons showed two- and three-bond couplings of 14.5 and 8.9 Hz, respectively.

Isolation of a mixture of *cis*-$[RuH_2(C{\equiv}CPh)(CO)(PPr^i_3)_2][K(18\text{-crown-}6)]$ (5) and *cis*-$[RuH_2(CPh{=}CH_2)(CO)(PPr^i_3)_2][K(18\text{-crown-}6)]$ (6)

$PhC{\equiv}CH$ (338 mg, 3.31 mmol) was added to a cold (−35 °C) solution of $[RuH_3(CO)(PPr^i_3)_2][K(18\text{-crown-}6)]$ (1000 mg, 1.32 mmol) in THF (3 mL). The mixture was left at −35 °C for 5 h. Addition of 12 mL of cold (−35 °C) hexane precipitated a white solid. It was isolated by filtration, washed with 3 × 3 mL of hexane and dried under vacuum. Yield: 684 mg (60%). IR (Nujol): $\nu_{C\equiv C}$ 2058, ν_{CO} and ν_{RhH} 1852, ν_{RuH} or/and $\nu_{C=C}$ 1597 cm^{-1}. **5**: ^{1}H NMR (200 MHz, THF-d$_8$): δ −11.10 (td, $^{2}J_{H-P} = 22.3$ Hz, $^{2}J_{H-H} = 7.0$, 1H, Ru*H*), −8.27 (td, $^{2}J_{H-P} = 26.1$ Hz, 1H, Ru*H*), 1.30 (dvt, $^{v}J_{H-P} = 6.3$ Hz, $^{3}J_{H-H} = 6.0$ Hz, 36H, C*H*$_3$), 2.21 (m, 6H, C*H*), 3.55 (s, 24H, crown-C*H*$_2$), 6.5–7.4 (m, 5H, C$_6$*H*$_5$). ^{31}P{^{1}H} NMR (80 MHz, THF-d$_8$): δ 84.0. ^{13}C{^{1}H} NMR (50 MHz, THF-d$_8$): δ 21.45, 21.61 (s, *C*H$_3$), 28.79 (vt, $^{v}J_{C-P} = 9.1$ Hz, P*C*H), 71.12 (s, crown-*C*H$_2$), 113.24 (s, ≡*C*Ph), 119.84, 127.64, 130.86 (s, *C*H, Ph), 135.30 (s, *C*$_{ipso}$, Ph), 148.24 (t, $^{2}J_{C-P} = 13.3$ Hz, Ru—*C*≡), 212.35 (t, $^{2}J_{C-P} = 9.5$ Hz, Ru—*C*O). **6**: ^{1}H NMR (200 MHz, THF-d$_8$): δ −12.39 (td, $^{2}J_{H-P} = 25.7$ Hz, $^{2}J_{H-H} = 7.0$, 1H, Ru*H*), −7.52 (td, $^{2}J_{H-P} = 27.8$ Hz, 1H, Ru*H*), 1.17 (dvt, $^{v}J_{H-P} = 6.3$ Hz, $^{3}J_{H-H} = 6.0$ Hz, 36H, C*H*$_3$), 2.12 (m, 6H, C*H*), 3.55 (s, 24H, crown-C*H*$_2$), 5.20, 5.55 (d, $^{2}J_{H-H} = 7.6$ Hz, 2H, =C*H*$_2$) 6.5–7.4 (m, 5H, C$_6$*H*$_5$). ^{31}P{^{1}H} NMR (80 MHz, THF-d$_8$): δ 81.2. ^{13}C{^{1}H} NMR (50 MHz, THF-d$_8$): δ 21.05, 21.97 (s, *C*H$_3$), 28.92 (vt, $^{v}J_{C-P} = 8.4$ Hz, P*C*H), 71.12 (s, crown-*C*H$_2$), 121.62 (t, $^{3}J_{C-P} = 2.1$ Hz, =*C*H$_2$), 120.40, 125.79, 128.93 (s, *C*H, Ph), 167.82 (s, *C*$_{ipso}$, Ph), 191.96 (t, $^{2}J_{C-P} = 9.3$ Hz, Ru—*C*Ph), 212.59 (t, $^{2}J_{C-P} = 10.5$ Hz, Ru—*C*O). Assignment of the ^{13}C signals is confirmed by an APT (attached proton test) experiment and comparison to the ^{13}C spectra of **4** and **7**.

Preparation of *cis*-[ReH$_2$(CCPh)(NO)(PPr$^{i}_{3}$)$_2$][K(18-crown-6)] (7)

PhC≡CH (145 mg, 1.42 mmol) was added to a solution of [ReH$_3$(NO)(PPr$^{i}_{3}$)$_2$][K(18-crown-6)] (600 mg, 0.71 mmol) in THF (6 mL). The mixture was stirred for 6 h. Addition of 20 mL of hexane precipitated a yellow solid. It was isolated by filtration, washed with 2 × 5 mL of hexane and dried under vacuum. Yield: 500 mg (75%). Anal. calcd for $C_{38}H_{75}KNO_7P_2Re$ (945.28): C, 48.28; H, 8.00; N, 1.48. Found: C, 47.89; H, 7.85; N, 1.54. IR (Nujol): ν_{ReH} 1790, ν_{ReH} or/and $\nu_{C=C}$ 1597, ν_{NO} 1500 cm^{-1}. ^{1}H NMR (200 MHz, THF-d$_8$): δ −5.45 (td, $^{2}J_{H-P} = 22.1$ Hz, $^{2}J_{H-H} = 8.3$, 1H, Re*H*), −3.78 (td, $^{2}J_{H-P} = 31.4$ Hz, 1H, Re*H*), 1.15, 1.19 (dvt, $^{v}J_{H-P} = 6.3$ Hz, $^{3}J_{H-H} = 5.3$ Hz, 36H, C*H*$_3$), 2.36 (m, 6H, C*H*), 3.57 (s, 24H, crown-C*H*$_2$), 4.81, 5.83 (d, $^{2}J_{H-H} = 7.1$ Hz, 2H, =C*H*$_2$) 6.60, 6.86, 7.40 (m, 5H, C$_6$*H*$_5$). ^{31}P{^{1}H} NMR (80 MHz, THF-d$_8$): δ 42.7. ^{13}C{^{1}H} NMR (50 MHz, THF-d$_8$): δ 20.78, 21.64 (s, *C*H$_3$), 29.51 (vt, $^{v}J_{C-P} = 10.1$ Hz, P*C*H), 71.12 (s, crown-*C*H$_2$), 120.30 (s, =*C*H$_2$), 121.18, 126.07, 128.96 (s, *C*H, Ph), 165.75 (s, *C*$_{ipso}$, Ph), 182.06 (t, $^{2}J_{C-P} = 5.0$ Hz, Re—*C*Ph). Assignment of the ^{13}C signals is confirmed by a gated-decoupled ^{13}C experiment: δ 120.30 (dd, $^{1}J_{C-H} = 142, 145$ Hz, =*C*H$_2$).

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