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

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Reactions of phenylacetylene with $[RuH_2(CO)L]^- [L is the pincer ligand C_6H_3-2,6-(CH_2PBu_2^i)_2], [RuH_3(CO)(PPr_3^i)_2]^- and [ReH_3(NO)(PPr_3^i)_2]^- have afforded the new anionc <math>\sigma$ -alkynyl and vinyl complexes *trans*-[RuH(C=CPh)(CO)L]^-, *cis*-[RuH_2(C=CPh)(CO)(PPr_3^i)_2]^-, *cis*-[RuH_2(CPh=CH_2)-(CO)(PPr_3^i)_2]^- and *cis*-[ReH_2(CPh=CH_2)(NO)(PPr_3^i)_2]^-, all as the [K(18-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*-[RuH₂(CO)L]⁻ (1)^{2a} [L is the pincer ligand C₆H₃-2,6-(CH₂PBu^t₂)₂], [RuH₃(CO)(PPrⁱ₃)₂]⁻ (2)^{2b} and [ReH₃(NO)-(PPrⁱ₃)₂]⁻ (3)^{2b} {all are [K(18-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 H₂/PhC₂⁻ 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.



A fast NMR tube reaction of *trans*-[RuH₂(CO)L]⁻ (1) and two equivalents of HC=CPh in pyridine-d₅ cleanly afforded a ruthenium product and one equivalent of H₂C=CHPh. The product could be isolated from pyridine or THF and characterized as *trans*-[RuH(CCPh)(CO)L]⁻ (4) by ¹H, ³¹P and ¹³C 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, $[RuH_3(CO)(PPr_3)_2]^-$ (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*-[RuH₂(C=CPh)(CO)(PPr_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*-[RuH₂(CPh=CH₂)(CO)(PPr_3)₂]⁻ (6) according to the ¹H and ¹³C NMR data.



Fig. 1 (A) Regular ¹H NMR and (B, C) difference NOE spectra of the acetylide 4. The RuH and $-C \equiv C - C_6 H_5$ fragments are *trans* since their enhancements in B and C originate from inequivalent CH₃ groups on the opposite sides of the P-C-P plane in 4. Solvent resonances (THF-d₈) are shown by stars, the one at δ 3.58 is overlapped with the intense line of [K(18-crown-6)]⁺.

Table 1	Selected	spectroscopic	data for comp	lexes 4–7
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Complex	δ(M-H)	δ(М-С≡)	δ(≡CPh)	$\delta(C_{ipso})$		
4^a 5^b	-9.67 -11.10 -8.27	151.59 148.24	113.88 113.24	134.91 135.30		
6	$\delta(M-H)$ -12.39 -7.52	$\delta(M-CPh)$	$\delta(=CH_2)$	$\delta(C_{ipso})$		
7	-5.45, -3.78	182.06	120.30	165.75		
$v_{C=C} = 2065 \text{ cm}^{-1}$. $v_{C=C} = 2058 \text{ cm}^{-1}$.						



Scheme 2

Finally, when rhenium trihydride, $[\text{ReH}_3(\text{NO})(\text{PPr}_3^i)_2]^-$ (3), was reacted with phenylacetylene, slow and clean formation of *cis*- $[\text{ReH}_2(\text{CPh}=\text{CH}_2)(\text{NO})(\text{PPr}_3^i)_2]^-$ (7) was complete in 6 h. No intermediates could be detected in the reaction solution by ³¹P NMR. The isolated product was characterized by ¹H, ³¹P and ¹³C NMR, IR spectroscopy, and elemental analysis. Facile protonation of 7 cleanly afforded a stable styrene complex, $\text{ReH}_2(\text{CH}_2=\text{CHPh})(\text{NO})(\text{PPr}_3^i)_2$, 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 $M-H^{\delta-\dots\delta^+}H-C$ hydrogen (also termed 'dihydrogen') bonding shown in Scheme 2.⁴ The experimental evidence for a reversible formation of the $[L_nM(\mu-H_2)CCPh]^-$ transient species is represented by the reported H/D scrambling in a FeH₂(dippe)₂/PhC=CD system.⁵ Scheme 2 shows further feasible rearrangements of $[L_nM(\mu-H_2)CCPh]^-$, which are either protonation of the metal fragment or hydride transfer to the C_{α} atom of phenylacetylene. An alternative C_{β} -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*-[RuH₂(CO)L]⁻ and two equivalents of DC=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-D} = 2.7 Hz) and



δ 5.12 (${}^{3}J_{\text{H-D}} = 1.6$ 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.

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){C₆H₃-2,6-(CH₂PBu¹₂)₂] [K(18-crown-6)] (4)

PhC≡CH (74 mg, 0.72 mmol) was added to a solution of $[RuH_2(CO){C_6H_3-2,6-(CH_2PBu_2^t)_2}][K(18-crown-6)]$ (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): $v_{C \equiv C}$ 2065 cm⁻¹, v_{C0} 1852 cm⁻¹, v_{RuH} 1583 cm⁻¹. ¹H NMR (200 MHz, THF-d₈): δ -9.67 (t, ²J_{H-P} = 21.7 Hz, 1H, Ru*H*), 1.22, 1.50 (vt, ^vJ_{H-P} = 5.6 Hz, 36H, CH₃), 3.07 (dvt, ²J_{H-H} = 14.9 Hz, ^vJ_{H-P} = 3.7 Hz, 2H, CH_2), 3.51 (s, 24H, crown- CH_2), 3.55 (overlapped with the crown resonance, 2H, CH₂), 6.31 (m, 1H, C₆H₃), 6.57 (m, 3H, Ar), 6.86 (m, 4H, C_6H_5). ³¹P{¹H} NMR (80 MHz, THF-d₈): δ 107.4. ¹³C{¹H} NMR (50 MHz, THF-d₈): δ 30.23, 29.88 (vt, ^vJ_{C-P} = 2.2 Hz, CH₃), 35.55 (vt, ^vJ_{C-P} = 8.1 Hz, PC), 37.61 (vt, ^vJ_{C-P} = 3.4 Hz, PC), 42.04 (vt, ^vJ_{C-P} = 10.0 Hz, PCH₂), 71.12 (s, crown-CH₂), 113.88 (s, \equiv CPh), 118.41 (vt, $^{v}J_{C-P} = 7.6$ Hz, CH, Ru-Ar), 120.13 (s, CH, Ru-Ar), 120.23, 127.41, 130.68 (s, CH, C₆H₅), 134.91 (s, C_{ipso} , C₆H₅), 149.04 (vt, ${}^{v}J_{C-P} = 10.3$ Hz, C, Ru–Ar), 151.59 (t, ${}^{2}J_{C-P} = 10.7$ Hz, Ru–C=), 188.57 (t, ${}^{2}J_{C-P} = 7.6$ Hz, RuC), 212.46 (t, ${}^{2}J_{C-P} = 10.1$ Hz, CO). Assignment of the 13 C signals was confirmed by gateddecoupled ¹³C NMR. Hydride-coupled ¹³C NMR: the carbonyl and ligand metal-bound carbon atoms both showed small ${}^{2}J_{C-H}$ 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-[RuH₂(C=CPh)(CO)(PPr₃)₂]-[K(18-crown-6)] (5) and cis-[RuH₂(CPh=CH₂)(CO)(PPr₃)₂]-[K(18-crown-6)] (6)

PhC=CH (338 mg, 3.31 mmol) was added to a cold $(-35 \,^{\circ}\text{C})$ solution of [RuH₃(CO)(PPrⁱ₃)₂][K(18-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): $v_{C \equiv C}$ 2058, v_{CO} and v_{RhH} 1852, v_{RuH} or/and $v_{c=c}$ 1597 cm⁻¹. 5: ¹H NMR (200 MHz, THF-d₈): δ -11.10 $(td, {}^{2}J_{H-P} = 22.3 \text{ Hz}, {}^{2}J_{H-H} = 7.0, 1\text{ H}, \text{ Ru}H), -8.27 \text{ (td,} {}^{2}J_{H-P} = 26.1 \text{ Hz}, 1\text{ H}, \text{ Ru}H), 1.30 \text{ (dvt, } {}^{v}J_{H-P} = 6.3 \text{ Hz},$ ${}^{3}J_{H-H} = 6.0$ Hz, 36H, CH₃), 2.21 (m, 6H, CH), 3.55 (s, 24H, crown-CH₂), 6.5–7.4 (m, 5H, C₆H₅). ³¹P{¹H} NMR (80 MHz, THF-d₈): δ 84.0. ¹³C{¹H} NMR (50 MHz, THF-d₈): δ 21.45, 21.61 (s, CH_3), 28.79 (vt, ${}^{v}J_{C-P} = 9.1$ Hz, PCH), 71.12 (s, crown-CH₂), 113.24 (s, ≡CPh), 119.84, 127.64, 130.86 (s, CH, Ph), 135.30 (s, C_{ipso} , Ph), 148.24 (t, ${}^{2}J_{C-P} = 13.3$ Hz, Ru $-C \equiv$), 212.35 (t, ${}^{2}J_{C-P} = 9.5$ Hz, Ru-CO). **6**: ¹H NMR (200 MHz, THF-d₈): $\delta - 12.39$ (td, ${}^{2}J_{H-P} = 25.7$ Hz, ${}^{2}J_{H-H} =$ 7.0, 1H, RuH), -7.52 (td, ${}^{2}J_{H-P} = 27.8$ Hz, 1H, RuH), 1.17 (dvt, ${}^{v}J_{H-P} = 6.3$ Hz, ${}^{3}J_{H-H} = 6.0$ Hz, 36H, CH₃), 2.12 (m, 6H, CH), 255 (c, 24.4) and 255 (c CH), 3.55 (s, 24H, crown-CH₂), 5.20, 5.55 (d, ${}^{2}J_{H-H} = 7.6$ Hz, 2H, =CH₂) 6.5-7.4 (m, 5H, C_6H_5). ³¹P{¹H} NMR (80 MHz, THF-d₈): δ 81.2. ¹³C{¹H} NMR (50 MHz, THF-d₈): δ 21.05, 21.97 (s, CH₃), 28.92 (vt, ${}^{v}J_{C-P} = 8.4$ Hz, PCH), 71.12 (s, crown-CH₂), 121.62 (t, ${}^{3}J_{C-P} = 2.1$ Hz, =CH₂), 120.40, 125.79, 128.93 (s, CH, Ph), 167.82 (s, C_{ipso} , Ph), 191.96 (t, ${}^{2}J_{C-P} = 9.3$ Hz, Ru–CPh), 212.59 (t, ${}^{2}J_{C-P} = 10.5$ Hz, Ru–CO). Assignment of the ¹³C signals is confirmed by an APT (attached proton test) experiment and comparison to the ¹³C spectra of 4 and 7.

Preparation of *cis*-[ReH₂(CCPh)(NO)(PPrⁱ₃)₂][K(18-crown-6)] (7)

PhC≡CH (145 mg, 1.42 mmol) was added to a solution of [ReH₃(NO)(PPr¹₃)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 C₃₈H₇₅KNO₇P₂Re (945.28): C, 48.28; H, 8.00; N, 1.48.

Found: C, 47.89; H, 7.85; N, 1.54. IR (Nujol): v_{ReH} 1790, v_{ReH} or/and $v_{C=C}$ 1597, v_{NO} 1500 cm⁻¹. ¹H NMR (200 MHz, THF-d₈): δ -5.45 (td, ²J_{H-P} = 22.1 Hz, ²J_{H-H} = 8.3, 1H, ReH), -3.78 (td, ²J_{H-P} = 31.4 Hz, 1H, ReH), 1.15, 1.19 (dvt, ^vJ_{H-P} = 6.3 Hz, ³J_{H-H} = 5.3 Hz, 36H, CH₃), 2.36 (m, 6H, CH), 3.57 (s, 24H, crown-CH₂), 4.81, 5.83 (d, ²J_{H-H} = 7.1 Hz, 2H, =CH₂) 6.60, 6.86, 7.40 (m, 5H, C₆H₅). ³¹P{¹H} NMR (80 MHz, THF-d₈): δ 42.7. ¹³C{¹H} NMR (50 MHz, THF-d₈): δ 20.78, 21.64 (s, CH₃), 29.51 (vt, ^vJ_{C-P} = 10.1 Hz, PCH), 71.12 (s, crown-CH₂), 120.30 (s, =CH₂), 121.18, 126.07, 128.96 (s, CH, Ph), 165.75 (s, C_{*ipso*}, Ph), 182.06 (t, ²J_{C-P} = 5.0 Hz, Re-CPh). Assignment of the ¹³C signals is confirmed by a gated-decoupled ¹³C experiment: δ 120.30 (dd, ¹J_{C-H} = 142, 145 Hz, =CH₂).

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