Syntheses and Reactions of Rhenium Vinylidene and Acetylide Complexes. Unprecedented Chirality Transfer through a C≡C Triple Bond

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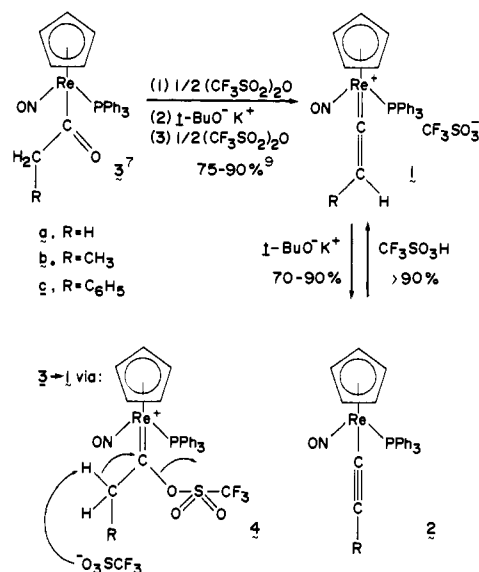
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There has been intense recent interest in the synthesis and reactivity of transition-metal alkylidene complexes (L_nM=CRR'),[2–4] vinylidene complexes (L_nM=C=CRR')[5] and other species containing metal–carbon multiple bonds.[6] We recently described the synthesis and isolation of the pseudotetrahedral electrophilic methylidene complex [(η-C$_5$H$_5$)Re(NO)(PPh$_3$)(=CH$_2$)]$^+$PF$_6^-$ and higher Re$^+$=CHR homologues.[3,4a,d] The latter were found to exist in two photointerconvertible geometrically isomeric forms and undergo stereospecific or highly stereoselective nucleophilic attack.[4] Hence we were interested in determining if similar phenomena could be observed in metallocumulene systems, which would have the carbon π terminus more remote from the metal site. In this communication, we describe (a) the facile synthesis of chiral rhenium vinylidene and acetylide complexes [(η-C$_5$H$_5$)Re(NO)(PPh$_3$)(=C=CRR')]$^+$X$^-$ (1) and (η-C$_5$H$_5$)Re(NO)(PPh$_3$)(C≡CR) (2) (R, R' = H, CH$_3$, C$_6$H$_5$), (b) the first observation of geometric isomerism in vinylidene complexes, (c) the thermal and photochemical interconversion of these isomers, (d) energy barriers associated with these isomerizations, and (e) stereospecific reactions of acetylide complexes 2 that entail *transfer of the metal chirality through a C≡C triple bond of formal cylindrical symmetry*!

Vinylidene complexes **1a–c** were prepared from the corresponding rhenium acyls (3) by a modification of the method of

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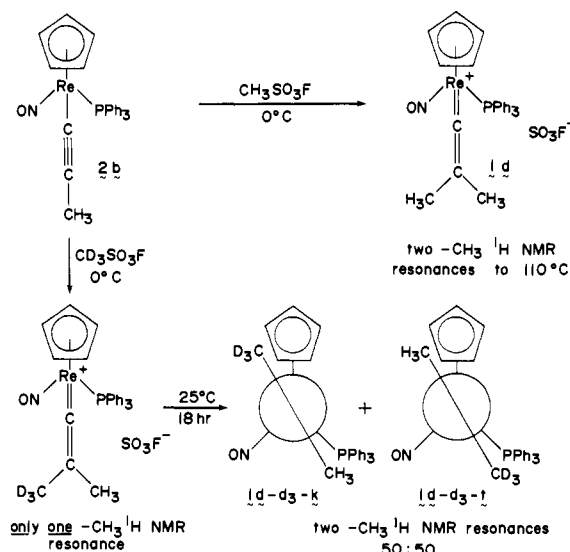
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Scheme I. Syntheses and Interconversions of Rhenium Vinylidene and Acetylide Complexes

Hughes,[5f–h] as shown in Scheme I.[7] The key step is thought to be fragmentation of the intermediate **4**. The CF$_3$SO$_3$H thus liberated protonates unreacted **3**, but this complication can be easily circumvented.[9]

The parent vinylidene [(η-C$_5$H$_5$)Re(NO)(PPh$_3$)(=C=CH$_2$)]$^+$CF$_3$SO$_3^-$ (**1a**) precipitated from CH$_2$Cl$_2$/hexane as a red powder. It exhibited *two* =CH$_2$ ^{1}H NMR resonances ((CDCl$_3$) δ 5.40, 4.94, both d, $J_{^1H–^1H'}$ = 20 Hz)[10] which did not coalesce (or undergo magnetization transfer)[11] at 110 °C (CDCl$_2$CDCl$_2$, 200 MHz). This bounds the Re$^+$=C=CH$_2$ rotational barrier, $\Delta G^{\ddagger}_{rot}$ (110 °C), as >18.6 kcal/mol. Substituted vinylidenes [(η-C$_5$H$_5$)Re(NO)(PPh$_3$)(=C=CHCH$_3$)]$^+$CF$_3$SO$_3^-$ (**1b**) and [(η-C$_5$H$_5$)Re(NO)(PPh$_3$)(=C=CHC$_6$H$_5$)]$^+$CF$_3$SO$_3^-$ (**1c**) were isolated from CH$_2$Cl$_2$ as light brown and golden crystals, respectively.[10] Both **1b** and **1c** existed in two isomeric forms (**k**, "kinetic"; **t**, "thermodynamic"; vide infra) which displayed distinct C$_5$H$_5$ and =CHR ^{1}H NMR resonances. Equilibrium ratios were (50 ± 2):(50 ± 2) (**1bk/1bt**) and (25 ± 2):(75 ± 2) (**1ck/1ct**).

Evidence was obtained that the two forms of **1b** and **1c** were *geometric* isomers that differed in the orientation of the =CHR group. First, irradiation of the (25 ± 2):(75 ± 2) **1ck/1ct** mixture (CD$_2$Cl$_2$, -78 °C, Hanovia 450-W lamp through Pyrex)[4c,d] gave a clean (50 ± 2):(50 ± 2) photostationary state. The sample was allowed to return to thermal equilibrium in the dark, and additional irradiation cycles were conducted without noticeable sample deterioration. Thus **1ck** and **1ct** can be photointerconverted analogously to C=C and Re$^+$=CHR geometric isomers.[4c,d] Second, both **1bk/1bt** and **1ck/1ct** were smoothly deprotonated by t-BuO$^-$K$^+$ to common products, the orange crystalline acetylides

(7) Starting acyls 3 were prepared in 65–85% yields by reaction of (η-C$_5$H$_5$)Re(NO)(PPh$_3$)(CO$_2$CH$_3$)[8] with RMgX. The physical and chemical properties of these complexes will be described in a subsequent full paper.

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(9) The first step of Scheme I yields (even with excess (CF$_3$SO$_2$)$_2$O) a 1:1 mixture of 1 and the protonated acyl [(η-C$_5$H$_5$)Re(NO)(PPh$_3$)(=C(OH)-CH$_2$R)]$^+$CF$_3$SO$_3^-$ (independently synthesized from the acyl and CF$_3$SO$_3$H). These cationic products are not separable in our hands. Addition of t-BuO$^-$K$^+$ deprotonates each (respectively) to a 1:1 mixture of acetylide (2) and 3. Subsequent addition of (CF$_3$SO$_2$)$_2$O at -78 °C converts this mixture *entirely* to 1, since the acetylide now acts as the base for the CF$_3$SO$_3$H liberated.

(10) Full characterization of **1a–e** and **2a–c** (^{1}H NMR, ^{13}C NMR, IR, and some mass spectral and microanalytical data) is given in the supplementary material. Selected key features include: ^{13}C NMR (ppm, CDCl$_3$) **1a–e** 327–336 (C$_\alpha$), 113–140 (C$_\beta$), **2a–c**, 111–123 (C$_\beta$), 71–92 (C$_\alpha$); IR (cm^{-1}, CHCl$_3$) **1a–e** $\nu_{N=O}$ 1735–1750 (s), $\nu_{C=C}$ 1645–1665 (w), **2a–c** $\nu_{N=O}$ 1655–1658 (s), $\nu_{C=C}$ 2020–2118 (w).

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Scheme II. Methylation of $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(C{\equiv}CCH_3)$ (2b)

Figure 1. Suggested means of chirality transfer from rhenium.

2b and **2c** (Scheme I).[10] The parent acetylide, $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(C{\equiv}CH)$ (**2a**, orange powder) was likewise available from the reaction of **1a** with $t\text{-}BuO^-K^+$.[10] Addition of CF_3SO_3H to **2a–c** re-formed the vinylidenes **1a–c** (Scheme I). Thus the $C{\equiv}C$ linkage in **2a–c**, like that in ynamines,[12] is *nucleophilic*. Davison and Selegue have noted similar reactivity with $(\eta\text{-}C_5H_5)Fe(L)_2(C{\equiv}CR)$ complexes.[5a–d]

Although $L_nM{=}C{=}CHR$ complexes have been prepared previously, geometric isomerism has not been heretofore noted. We suggest that the two isomers of **1b** (and **1c**) have their ${=}CHR$ planes essentially parallel to the Re–PPh$_3$ bond but differ as shown in Newman projections (down the $>C{=}C{=}Re^+$ bond) I and II.

$\mathbf{I}$ $\angle N\text{-}Re\text{-}P = 90 \pm 2°$ $\mathbf{II}$
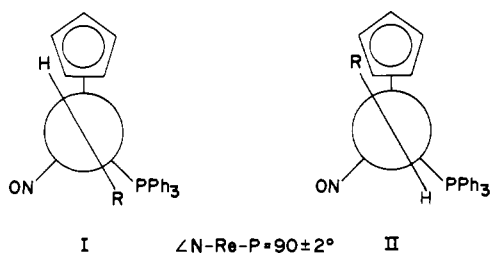
Our reasoning is as follows: (a) the X-ray structure of benzylidene $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)({=}CHC_6H_5)]^+PF_6$ shows the ${=}CHR$ plane to be parallel to the Re–NO bond;[4d] (b) X-ray structures of the $M{=}(C)_x{=}CR_2$ series $(\eta\text{-}C_5H_5)Mn(CO)_2({=}C(CH_3)_2),$[2d] $(\eta\text{-}C_5H_5)Mn(CO)_2({=}C{=}C(CH_3)_2),$[5j] and $(\eta\text{-}C_5H_5)Mn(CO)_2({=}C{=}C{=}C(C_6H_5)_2)$[6b] show that neighboring homologues have orthogonal carbon π termini; (c) since the $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)$ fragment HOMO is a d orbital whose mirror plane (bisecting all four lobes) contains the Re–PPh$_3$ bond,[4d] geometries I and II maximize vinylidene π bonding.

While K_{eq} for **1bk** $\rightleftharpoons$ **1bt** $\simeq$ 1 and K_{eq} for **1ck** $\rightleftharpoons$ **1ct** $\simeq$ 3, K_{eq} for the geometric isomers of the homologous alkylidene complexes $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)({=}CHCH_3)]^+PF_6^-$ and $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)({=}CHC_6H_5)]^+PF_6^-$ are ca. 10 and $\gtrsim$99, respectively.[4a,d] This indicates that the vinylidene ${=}CHR$ moiety is better insulated from the steric environment of the metal than the alkylidene ${=}CHR$ moiety. Hence the β carbons of **1** and **2** were considered to be unlikely sites for stereospecific reactions. Surprisingly, the following results show this presumption to be incorrect.

Methyl acetylide **2b** was treated with CH_3SO_3F in CD_2Cl_2 at -78 °C (Scheme II). ^1H NMR monitoring showed that dimethylvinylidene $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)({=}C{=}C(CH_3)_2)]^+SO_3F^-$ (**1d**) formed cleanly upon warming to 0 °C. Complex **1d** exhibited *two* CH$_3$ ^1H NMR resonances (δ 1.96, 1.24) and was isolated as yellow crystals from CH_2Cl_2/ether.[10] Similar reaction
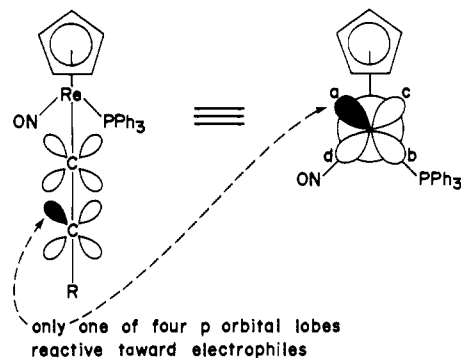
of **2b** with CD_3SO_3F gave **1d**-d_3, but the expected δ 1.96 ^1H NMR resonance was *absent* (detection limit 1%). Thus only one geometric isomer, **1d**-d_3-k, formed initially. As the sample was warmed to >0 °C, the missing resonance appeared as the δ 1.24 resonance diminished. After 18 h at 25 °C, both CH$_3$ resonances (and hence both **1d**-d_3 isomers) were present in equal amounts (Scheme II).

The generality of this phenomenon was probed with additional acetylides and electrophiles. A similar reaction of **2b** with CF_3SO_3H at -78 °C gave a $(90 \pm 2):(10 \pm 2)$ **1bk/1bt** mixture. Equilibration to a $(50 \pm 2):(50 \pm 2)$ thermodynamic mixture occurred over 12 h at 25 °C. Reaction of phenyl acetylide **2c** with CF_3SO_3H at -78 °C gave a $\gtrsim$99:1 **1ck/1ct** mixture. Equilibration to a $(25 \pm 2):(75 \pm 2)$ thermodynamic mixture required ca. 3 h at 25 °C. Reaction of **2c** with CH_3SO_3F at 0 °C gave a single isomer of the disubstituted vinylidene $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)({=}C{=}C(CH_3)C_6H_5)]^+SO_3F^-$ (**1ek**).[10] The rate of equilibration of **1ek** to a $(25 \pm 2):(75 \pm 2)$ **1ek/1et** mixture was measured 30, 35, 40, and 45 °C and gave the activation parameters $\Delta H^{\ddagger}_{rot} = 15.7 \pm 1.7$ kcal/mol and $\Delta S^{\ddagger}_{rot} = -9.8 \pm 5.5$ eu.[13]

Thus, of the two possible orientations about the allene-like axis of chirality in **1b–e**, only one is (initially) obtained when electrophiles attack **2**. In essence, the rhenium chirality is transmitted through the formally cylindrically symmetrical bond. Such stereospecificity is to our knowledge unprecedented.

Our tentative interpretation of the origin of this asymmetric induction is shown schematically in Figure 1. Of the four p lobes available on the acetylide terminus for electrophile attack, two (c, d) are orthogonal to the d donor orbital on rhenium and thus by analogy to structurally constrained enamines[14] should be unreactive. Of the remaining lobes a and b, we favor electrophile attack upon a since this would be anti to the bulky PPh$_3$ ligand. An important expected (and observed) consequence is that whenever the entering electrophile is smaller than the acetylide R group, the vinylidene geometric isomer formed kinetically should not be the thermodynamically favored one. On this basis, we assign (1) **1bk** and **1ck** the structure I (R = CH$_3$,C$_6$H$_5$), (2) **1bt** and **1ct** the structure II, (3) **1d**-d_3 isomers the structures shown in Scheme II, and (4) **1ek** a structure with CH$_3$ anti and C$_6$H$_5$ syn to the PPh$_3$.

The closest analogy of which we are aware for this type of asymmetric induction would be the reaction of chiral R—C${\equiv}$C—CHRX* systems with aluminum hydrides to give (via a net S_N2' displacement) chiral allenes.[15] However, vinylalane intermediates have been implicated in this transformation; furthermore, it entails only the conversion of a chiral center to a chiral axis, rather than the creation of a new element of chirality as in

(13) No coalescence was observed up to 110 °C in the 200-MHz ^1H NMR spectra of **1bk/1bt**, **1ck/1ct**, and **1d**; this bounds $\Delta G^{\ddagger}_{rot}$ (110 °C) for these compounds as $\gtrsim$18 kcal/mol. Data on homologous alkylidene complexes include $\Delta G^{\ddagger}_{rot}$ (27 °C) >15 kcal/mol for $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)({=}CH_2)]^+PF_6^-$[3b,4d] and $\Delta H^{\ddagger}_{rot} = 20.9$ kcal/mol and $\Delta S^{\ddagger}_{rot} = -3.8$ eu for sc-$[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)({=}CHC_6H_5)]^+PF_6^-$.[4c,d]

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Scheme II. In summary, this study has provided another striking example of the unique capabilities of chiral transition-metal centers in stoichiometric asymmetric synthesis and foreshadows a much broader range of reactions that will be possible with $(\eta\text{-}C_5H_5)\text{-}Re(NO)(PPh_3)$ systems.

Supplementary Material Available: Characterization of **1a–c** and **2a–c** (5 pages).[10] Ordering information is given on any current masthead page.

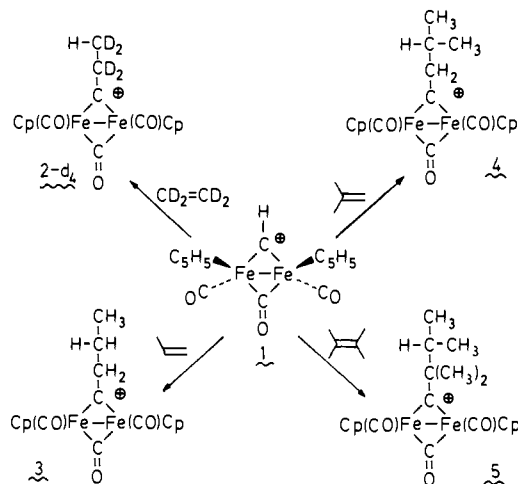## Hydrocarbation: Addition of the C–H Bond of a Cationic Bridging Iron–Methylidyne Complex to Alkenes

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The addition of element-to-hydrogen bonds to alkenes is a fundamental step in many catalytic and stoichiometric transformations.[1] The synthetic utility of this general reaction type is exemplified by the hydroboration[2] and hydrozirconation[3] reactions. Here we report that the bridging iron–methylidyne complex [cis-$Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH)]^+PF_6^-$ (**1**)[4] (Cp = η-C_5H_5) reacts with a variety of alkenes to add the methylidyne *carbon–hydrogen* bond across the carbon–carbon double bond. This "hydrocarbation" reaction provides an unprecedented method for carbon–carbon bond formation. Metal-bound methylidyne ligands have been proposed as intermediates in the catalytic reduction of CO,[5] and addition of a methylidyne C–H bond to an alkene is a potential homologation step in these processes.

The cationic iron–methylidyne complex **1** can be viewed as a relatively stable secondary carbonium ion stabilized by electron donation from the two iron centers.[6] Complex **1** is synthesized from the bridging methylene complex $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)^{4,7}$ by hydride abstraction with $(C_6H_5)_3C^+PF_6^-$ and is consequently a more stable cation than the triphenylmethyl cation. In spite of its relative thermodynamic stability, the methylidyne complex **1** is a very reactive electrophile and forms stable adducts with $N(CH_3)_3$, $(CH_3)_3CO^-$, and CO by addition of the nucleophile to the methylidyne carbon[7b,8] as well as reacting with alkenes as described here.

When a slurry of the red iron–methylidyne complex **1** in CH_2Cl_2 was stirred under an ethylene atmosphere and warmed from –78 °C to room temperature, a maroon crystalline product was formed. Evaporation of solvent in vacuo followed by recrystallization of the product from acetone–ether gave the propylidyne complex [cis-$Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_2CH_3)]^+PF_6^-$ (**2**) in 65% yield.[9,10] The spectroscopic properties of **2** are comparable to those of related cationic iron carbyne complexes which were first prepared by Nitay et al.[6a]

The reaction of **1** with excess ethylene in CD_2Cl_2 at –20 °C was monitored by ^{1}H NMR spectroscopy. The time for 50% conversion of **1** to **2** was approximately 15 min at –20 °C, and no detectable intermediates or side reactions were noted. Furthermore, we have never observed further reaction of alkenes with the alkylidyne hydrocarbation products (vide infra).[11] Thus, the methylidyne C–H bond of **1** has unique reactivity not possessed by the C–CH_2CH_3 bond of **2**; similar observations have been made in the cases of hydroboration and hydrozirconation.[2,3]

The reaction of **1** with $CD_2=CD_2$ (>95% deuterated) in CD_2Cl_2 gives 2-d_4 in which >90% of the proton originally bonded to the methylidyne carbon of **1** has been delivered to the methyl group of 2-d_4 as determined by ^{1}H NMR spectroscopy.[12] This establishes that **2** is formed by 1,2-addition of carbon and hydrogen to ethylene and rules out the possibility that **2** arises by electrophilic addition of **1** to ethylene followed by two sequential 1,2 hydrogen shifts in an intermediate such as I.

† National Science Foundation Postdoctoral Fellow.

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(8) Fagan, P. J.; Casey, C. P., unpublished results.

(9) **2**: ^{1}H NMR (acetone-d_6) δ 5.66 (10 H, s, Cp), 5.46 (2 H, q, J = 6.6 Hz, CH_2), 1.81 (3 H, t, J = 6.6 Hz, CH_3); ^{13}C{^{1}H}NMR (acetone-d_6) δ 504.7 (μ-C^+), 252.4 (μ-CO), 208.9 (CO), 93.1 (Cp), 70.6 (CH_2), 16.2 (CH_3); IR (Nujol) 2040 (s), 2005 (m), 1855 (s) cm⁻¹. Anal. Calcd for $C_{16}H_{15}O_3PF_6Fe_2$: C, 37.54; H, 2.95; P, 6.05. Found: C, 37.88; H, 3.22; P, 5.99.

(10) The complex [cis-$Cp_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_3)]^+BF_4^-$, which has been characterized by X-ray crystallography and contains cis-carbonyl ligands, has an IR spectrum similar to that of **2**.[6b]

(11) A similar lack of reactivity has been noted for the complex [cis-$Cp_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_3)]^+BF_4^-$, which will only react with propene photochemically: Dyke, A. F.; Guerchais, J. E.; Knox, S. A. R.; Roue, J.; Short, R. L.; Taylor, G. E.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1981**, 537–538.

(12) 2-d_4: ^{1}H NMR (acetone-d_6) δ 5.66 (10 H, s, Cp), 1.75 (1 H, br s, CD_2H). Integration of the resonance due to the CD_2H group relative to the area under the expected region for a CDH resonance sets a lower limit of 90% for incorporation of the proton into the CD_2H group.