°C for the region δ +1 to −10. The sample was then removed from the probe and cooled to −78 °C. Solid $PPh_2(2\text{-}MeC_6H_4)$ (0.0119 g) was added to this sample. The sample was then shaken for 30 s, returned to the probe at −20 °C, and allowed to equilibrate, and the NMR spectrum was recorded. The sample was removed and cooled to −78 °C, an additional amount of ligand (0.0108 g) was added, and the NMR spectrum was recorded. This was repeated several more times. The shift of the $Pt_2(\mu\text{-}H)$ proton was then used to calculate K from a nonlinear regressive fit of the observed shift vs. $[L]^0/[Ia]^0$ curve.[52] The value thus obtained was 3.2 L mol^{-1}. This procedure was repeated at 0 °C to give K = 1.9 L mol^{-1}.

Kinetics of Dissociation of PPh_3 from Complex IIIa. A sample of complex Ia in CD_2Cl_2 (0.18 M) in an NMR tube was cooled to −90 °C in the probe of the NMR spectrometer, and the spectrum was recorded. PPh_3 was added as a solid to give a 0.20 M solution. The cold tube was shaken to give a homogeneous solution, being careful to keep it cold, and was returned to the NMR probe at −90 °C. The spectrum was recorded, and further spectra were obtained at 10 °C intervals as the probe was slowly warmed. Lifetimes were calculated from the spectra at each temperature. A similar experiment was carried out by using ^{31}P NMR spectroscopy.

Acknowledgment. We thank NSERC (Canada) for financial support.

Registry No. Ia, 65911-00-2; IIa, 77275-76-4; IIe, 86528-20-3; $IIe^+PF_6^-$, 86528-26-9; IIf, 86528-21-4; $IIf^+PF_6^-$, 86528-27-0; IIg, 86528-28-1; $IIg^+PF_6^-$, 86528-29-2; IIIa, 86528-22-5; IIIc, 86528-23-6; IIId, 86528-24-7; IIIf, 86528-25-8; H_2, 1333-74-0; deuterium, 7782-39-0.

Supplementary Material Available: Table I, spectroscopic data for complexes II and Figures 3, Arrhenius plot for dissociation of IIIa, 5, observed points and best fit lines in graphs of absorbance vs. $[L]^0/[Ia]^0$, 6, changes in absorption spectrum for reaction of Ia with PPh_3 at 25 °C, 8, Arrhenius plots for reactions of eq 3, and 9, changes in absorption spectrum for reaction of Ia with PPh_3 at 4 °C (8 pages). Ordering information is given on any current masthead page.

Syntheses, Properties, and X-ray Crystal Structures of Stable Methylidene Complexes of the Formula $[(\eta\text{-}C_5Me_5)Re(NO)(L)(=CH_2)]^+PF_6^-$

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Abstract: Reaction of $Re_2(CO)_{10}$ with pentamethylcyclopentadiene at 150–210 °C yields $(\eta\text{-}C_5Me_5)Re(CO)_3$ (**6**). Treatment of **6** with $NO^+BF_4^-$ gives $[(\eta\text{-}C_5Me_5)Re(NO)(CO)_2]^+BF_4^-$ (**7**). Reaction of **7** with $C_6H_5I^+\text{–}O^-/CH_3CN$ yields $[(\eta\text{-}C_5Me_5)Re(NO)(CO)(NCCH_3)]^+BF_4^-$ (**8**), which is subsequently treated with L (**a**, L = PPh_3; **b**, L = $P(OPh)_3$) to give $[(\eta\text{-}C_5Me_5)Re(NO)(L)(CO)]^+BF_4^-$ (**9a**, **9b**). Reduction of **9a** and **9b** with $Li(C_2H_5)_3BH/BH_3$ and $NaBH_4$, respectively, yields $(\eta\text{-}C_5Me_5)Re(NO)(L)(CH_3)$ (**10a**, **10b**). When **10a** and **10b** are treated with $Ph_3C^+PF_6^-$, the stable (>100 °C as solids) methylidene complexes $[(\eta\text{-}C_5Me_5)Re(NO)(PPh_3)(=CH_2)]^+PF_6^-$ (**4**) and $[(\eta\text{-}C_5Me_5)Re(NO)(P(OPh)_3)(=CH_2)]^+PF_6^-$ (**5**) form. Properties of the $=CH_2$ ligands in **4** and **5** are studied in detail: $\Delta G^{\ddagger}_{rot}$ (~114 °C) $\gtrsim$ 19 kcal/mol; IR $\nu_{=CH_2}$: **4**, 2987/2972 and 2922 cm^{-1}; **5**, 2987/2976 and 2920 cm^{-1}; $\nu_{=CD_2}$: **4**-d_2, 2246/2239 and 2181 cm^{-1}; **5**-d_2, 2245/2238 and 2187 cm^{-1}; NMR $^1J_{^{13}C-^1H}$(**5**) = 154 and 143 Hz. The −160 °C X-ray crystal structure of **4** shows $=CH_2/NO$ disorder. The room-temperature X-ray crystal structure of **5** indicates space group $P2_1/c$, a = 8.666 (3) Å, b = 12.387 (5) Å, c = 34.90 (1) Å, β = 102.34 (3)°, V = 3360 (2) Å^3, Z = 4, ρ_{calcd} = 1.82 g cm^{-3}. For 3038 reflections ($I_o \geq 3.0\sigma(I_o^2)$), R = 0.057 and R_w = 0.064. The $Re{=}CH_2$ bond length is 1.898 (18) Å, and the $=CH_2$ plane is essentially parallel to the Re–NO bond. This provides optimal overlap with the d orbital HOMO on rhenium.

The synthesis, isolation, and characterization of transition-metal methylidene complexes, $L_nM{=}CH_2$, have been highly sought objectives of organometallic chemists over the past two decades. In addition to the intrinsic interest in stabilizing the normally reactive CH_2 moiety,[3] $L_nM{=}CH_2$ species play key roles in metal-catalyzed olefin metathesis[4] and olefin cyclopropanation.[5]

Some of the earliest attempts to prepare transition-metal methylidene complexes came from the laboratories of Pettit[6] and Green.[7] These investigators found that the addition of acid to $(\eta\text{-}C_5H_5)Fe(CO)_2(CH_2OCH_3)$ gave a species that could convert cyclohexene to norcarane. The intermediacy of $[(\eta\text{-}C_5H_5)Fe(CO)_2(=CH_2)]^+$ (**1**) was proposed. However, workup of the reaction mixture afforded mainly ethylene complex $[(\eta\text{-}C_5H_5)Fe(CO)_2(H_2C{=}CH_2)]^+$. Brookhart subsequently found that **1** was too unstable to be observed by ^1H NMR at −80 °C.[8]

Herrmann has studied the reaction of $(\eta\text{-}C_5H_4R)Mn(CO)_2(THF)$ with CH_2N_2.[9] No $(\eta\text{-}C_5H_4R)Mn(CO)_2(=CH_2)$ was detected, but the plausible methylidene decomposition products $(\eta\text{-}C_5H_4R)Mn(CO)_2(H_2C{=}CH_2)$ and $(\eta\text{-}C_5H_4R)(CO)_2Mn\text{-}CH_2\text{-}Mn(CO)_2(\eta\text{-}C_5H_4R)$ were isolated. The latter was the first example of a bridging CH_2 complex. Such species are now relatively common.[10]

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The first isolable methylidene complex, $(\eta\text{-}C_5H_5)_2Ta(CH_3)(=CH_2)$ (**2**), was reported in a landmark communication by Schrock in 1975.[11] It was prepared by deprotonation of $[(\eta\text{-}C_5H_5)_2Ta(CH_3)_2]^+$ and exhibited reactivity indicative of a *nucleophilic* $=CH_2$ moiety. This is characteristic of all early transition-metal alkylidene complexes synthesized to date. The unstable methylidene $(\eta\text{-}C_5H_5)_2Zr(PPh_2Me)(=CH_2)$ has been briefly described by Schwartz.[12]

Stable methylidene complexes of the middle and late transition metals have proven to be more elusive.[13] In 1980, Brookhart and Flood reported the generation of the labile methylidene $[(\eta\text{-}C_5H_5)\overline{FeP(C_6H_5)_2CH_2CH_2P}(C_6H_5)_2(=CH_2)]^+$.[14] Subsequently, spectroscopically detectable $[(\eta\text{-}C_5H_5)Mo(CO)_2(L)(=CH_2)]^+$ and $[(\eta\text{-}C_5H_5)W(CO)_2(L)(=CH_2)]^+$ species were synthesized.[15] In 1981, Schrock reported that methylidyne $W(PMe_3)_4(Cl)(\equiv CH)$ could be protonated to give the crystalline T-shaped methylidene $[W(PMe_3)_4(Cl)(=CH_2)]^+CF_3SO_3^-$.[16]

In 1979, we reported the synthesis and some chemical properties of the electrophilic rhenium methylidene $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(=CH_2)]^+PF_6^-$ (**3**).[17] Although **3** rapidly self-coupled to form ethylene complex $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C=CH_2)]^+PF_6^-$ at room temperature,[18] it proved isolable as a powder at −23 °C.[19] The mechanism of this coupling is the subject of the following paper.[18] In view of the demonstrated ability of the pentamethylcyclopentadienyl ligand to kinetically stabilize organometallic complexes,[20] we undertook a study of C_5Me_5 homologues of **3**.

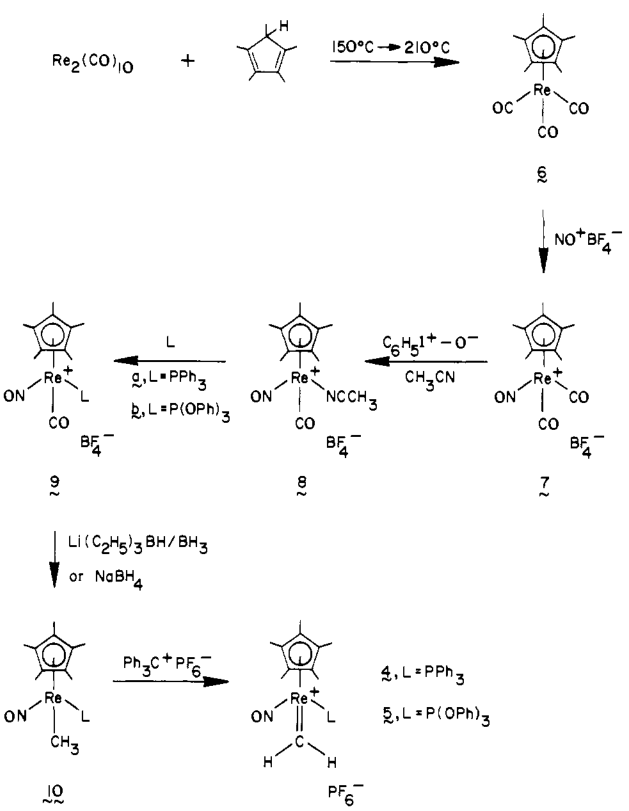
In this paper we report (a) facile, high-yield syntheses of methylidene complexes $[(\eta\text{-}C_5Me_5)Re(NO)(L)(=CH_2)]^+PF_6^-$ (**4**, L = PPh_3; **5**, L = $P(OPh)_3$), which are stable as solids to >100 °C, (b) X-ray crystal structures of **4** and **5**, and (c) a thorough study of the physical properties of the $=CH_2$ ligand in **4** and **5**.

Results

Synthesis of Methylidene Complexes. The preparation of methylidenes $[(\eta\text{-}C_5Me_5)Re(NO)(PPh_3)(=CH_2)]^+PF_6^-$ (**4**) and $[(\eta\text{-}C_5Me_5)Re(NO)(P(OPh)_3)(=CH_2)]^+PF_6^-$ (**5**) paralleled the route developed for the synthesis of $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(=CH_2)]^+PF_6^-$ (**3**).[19] Direct reaction of $Re_2(CO)_{10}$ with pentamethylcyclopentadiene afforded $(\eta\text{-}C_5Me_5)Re(CO)_3$ (**6**) in 95% yield (Scheme I). This constituted a distinct improvement over the literature procedures.[21]

Addition of $NO^+BF_4^-$ to **6** gave the cation $[(\eta\text{-}C_5Me_5)Re(NO)(CO)_2]^+BF_4^-$ (**7**) in 95% yield (Scheme I). While the crystallographic portion of this study was in progress, a similar synthesis of the PF_6^- salt of **7** was reported by Graham and Sweet.[22] A CO ligand was oxidatively displaced from **7** with $C_6H_5I^+\text{–}O^-/CH_3CN$. This gave $[(\eta\text{-}C_5Me_5)Re(NO)(CO)(NCCH_3)]^+BF_4^-$ (**8**) in 91% yield. Reaction of **8** with $P(OPh)_3$ in refluxing THF gave $[(\eta\text{-}C_5Me_5)Re(NO)(P(OPh)_3)(CO)]^+BF_4^-$ (**9b**) in 76% yield. The PPh_3 complex $[(\eta\text{-}C_5Me_5)Re(NO)(PPh_3)(CO)]^+BF_4^-$ (**9a**) was similarly prepared from **7** in 85% overall yield but without the isolation of intermediate **8**.

Scheme I. Syntheses of Methylidene Complexes $[(\eta\text{-}C_5Me_5)Re(NO)(L)(=CH_2)]^+PF_6^-$



The CO ligand in **9** was reduced to a CH_3 ligand by $Li(C_2H_5)_3BH/BH_3$ (**9a**) or $NaBH_4$ in THF (**9b**). Alkyls $(\eta\text{-}C_5Me_5)Re(NO)(PPh_3)(CH_3)$ (**10a**) and $(\eta\text{-}C_5Me_5)Re(NO)(P(OPh)_3)(CH_3)$ (**10b**) were isolated in 73% and 64% yields, respectively. The former reaction proceeds via the stable formyl $(\eta\text{-}C_5Me_5)Re(NO)(PPh_3)(CHO)$.

Treatment of **10a** and **10b** with $Ph_3C^+PF_6^-$ gave methylidenes **4** and **5** in 70% and 76% isolated yields, respectively. As solids, **4** and **5** were thermally stable to ≥115 °C and were moderately air stable. In CD_3CN, **5** (ca. 0.11 M) showed ca. 30% decomposition (relative to Ph_3SiCH_3 standard) after 1 h at 60 °C. Spectroscopic properties of **4** and **5**, as well as precursors **7**–**10**, are summarized in Table I.

Spectroscopic Properties of Methylidene Ligands. Spectroscopic features of methylidenes **4** and **5** were studied in detail. Both **4** and **5** exhibited downfield ^1H NMR resonances characteristic of electrophilic $=CHR$ complexes[7,14,15,17,23] and separate resonances for each of the $=CH_2$ hydrogens. No coalescence or broadening of these resonances was observed at 114 °C in the 80-MHz spectrum of **4** in $CDCl_2CDCl_2$. Similarly, there were no significant changes in the 90-MHz ^1H NMR spectrum of **5** at 107 °C. These data bound the energy barrier for $=CH_2$ rotation, $\Delta G^{\ddagger}_{rot}$ (~114 °C), as $\gtrsim 19$ kcal/mol. Selective saturation of one $=CH_2$ resonance of **4** or **5** (87 °C) did not significantly affect the intensity of the other resonance (<10% intensity change). Hence the spin saturation transfer method[24] could not be used to determine $\Delta G^{\ddagger}_{rot}$.

The ^{13}C NMR spectra of **4** and **5** exhibited characteristic downfield $=CH_2$ resonances (Table I). The $^{13}C\{^{31}P\}$ NMR spectrum of **5** showed a doublet of doublets for the $=CH_2$ carbon.

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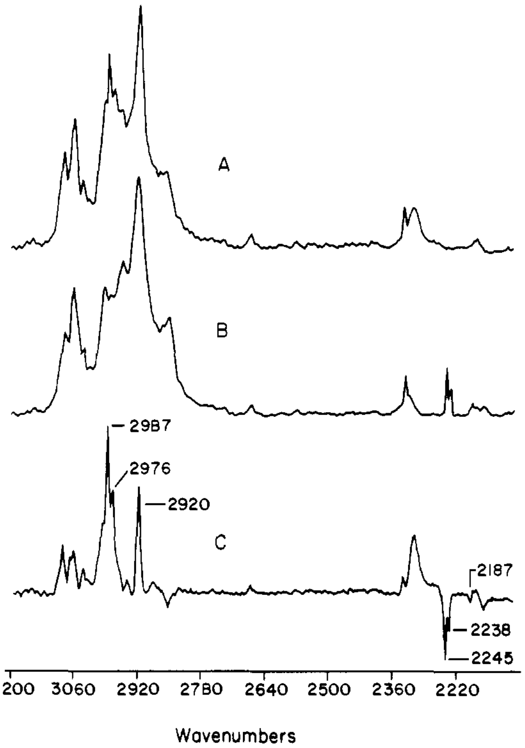

Figure 1. Absorbance FT IR spectra of **5** and **5**-d_2 (KBr): trace A, **5**; trace B, **5**-d_2; trace C, difference spectrum, A − B.

Values of 154 and 143 Hz were found for $^1J_{^1H_\alpha-^{13}C}$ and $^1J_{^1H_\alpha'-^{13}C}$.

Samples of (η-C_5Me_5)Re(NO)(PPh_3)(CD_3) (**10a**-d_3) and (η-C_5Me_5)Re(NO)($P(OPh)_3$)(CD_3) (**10b**-d_3) were prepared by the sequential treatment of **9a** and **9b**, respectively, with Li(C_2H_5)$_3$BD and BD_3·$S(CH_3)_2$. These were reacted with $Ph_3C^+PF_6^-$ to give the deuterated methylidenes **4**-d_2 and **5**-d_2. The FT IR spectra of **5** and **5**-d_2 were recorded in KBr (Figure 1, traces A and B). Trace B was subtracted from trace A to give a difference spectrum (trace C). The $=CH_2$ ν_{C-H} were assigned as 2987/2976 and 2920 cm^{-1}, and the $=CD_2$ ν_{C-D} were assigned as 2245/2238 and 2187 cm^{-1}. The IR spectra of **4** and **4**-d_2 were strikingly similar to those in Figure 1. The corresponding absorptions were found at (**4**) 2987/2972 and 2922 cm^{-1} and (**4**-d_2) 2246/2239 and 2181 cm^{-1}.

X-ray Crystal Structures of 4 and 5. In order to establish the Re=CH_2 bonding geometry, X-ray structural studies were undertaken. The **10a**/$Ph_3C^+PF_6^-$ reaction mixture (Scheme I; −78 °C, $CHCl_2CH_3$) was carefully layered with hexane. Crystals of **4** formed (−15 °C, 2 days), and a brown triangular prism was selected and mounted on a glass fiber. X-ray data were collected on a Syntex P$\bar{1}$ automated diffractometer under conditions summarized in Table II. The general techniques employed have been previously described.[25] Lattice parameters (Table II) were determined by using 15 centered reflections with 2θ between 10° and 24°. Of 3789 unique reflections with $2\theta < 45°$, 2891 with $I \geq 3\sigma(I)$ were used in the final refinement.[25c] The position of the rhenium atom was obtained from a three-dimensional Patterson map. Several cycles of full-matrix refinement were followed by computation of an electron density difference map. All nonhydrogen atoms were located. Anomalous dispersion corrections were applied throughout the refinement. An absorption correction was applied, after which most of the hydrogen atoms, except for those of the $=CH_2$, could be located in the electron density difference map.

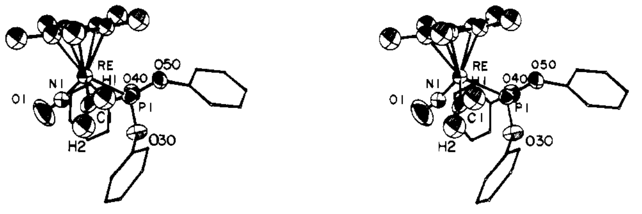

Figure 2. Stereoview of the molecular structure of [(η-C_5Me_5)Re(NO)($P(OPh)_3$)(=CH_2)]$^+PF_6^-$·$CHCl_2CH_3$ (**5**·$CHCl_2CH_3$). The PF_6^-, $CHCl_2CH_3$, and phenyl ring thermal ellipsoids have been omitted for clarity.

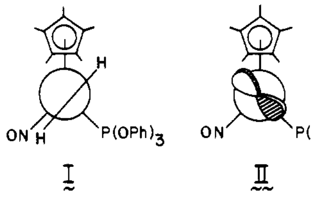

Figure 3. Newman projections of the X-ray crystal structure of **5**·$CHCl_2CH_3$ (I) and the [(η-C_5Me_5)Re(NO)($P(OPh)_3$)]$^+$ fragment HOMO (II).

At this point, examination of an electron density map showed that the NO and $=CH_2$ ligands were disordered. The configuration of ligands that had been assigned was superimposed upon a second configuration in which these two ligands had exchanged places. A model of this disorder was incorporated into the refinement.[26]

One hydrogen atom from each methyl group was assigned a position indicated by the electron difference map. The other methyl hydrogens and phenyl hydrogens were held at computed positions (C–H = 1.0 Å). Hydrogen atoms were assigned isotropic thermal parameters ($-CH_3$, B = 3.0; $-C_6H_5$, B = 2.0). The rhenium, phosphorus, and fluorine atoms were refined with anisotropic Gaussian thermal amplitudes. All other atoms were refined with isotropic thermal parameters. After several cycles of such full-matrix refinement, an R index of 0.040 and a R_w of 0.049 were obtained.[27] A difference map with a $(\sin\theta)/\lambda$ cutoff of 0.35[28] showed no identifiable $=CH_2$ hydrogen atoms. Since the $=CH_2$/NO disorder undoubtedly contributed to the inability to locate the $=CH_2$ hydrogens, we sought to determine the X-ray crystal structure of a homologue of **4**.

When a $CHCl_2CH_3$ solution of **5** was layered with petroleum ether (bp 20–40 °C) and stored at −15 °C under O_2-free conditions, crystals of **5**·$CHCl_2CH_3$ suitable for X-ray analysis were obtained. Several attempts were made to collect data at −160 °C, but as the crystals cooled, they cracked and were no longer single. Finally, data were collected at room temperature as outlined above and in Table II. The lattice parameters (Table II) were determined by using 15 centered reflections with 2θ between 9° and 34°. Of the 5938 reflections with $2\theta < 50°$, 3038 with $I \geq 3\sigma(I)$ were used in the final refinement.[25c] The positions of all non-hydrogen atoms were determined as described for **4**. An absorption correction was applied, after which most of the hydrogen atoms could be located from a difference map. The $=CH_2$ hydrogens and one hydrogen from each methyl group were held at positions indicated in the difference map. Other hydrogens were held at computed positions (C–H = 1.0 Å). Hydrogen atoms

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(26) Two =C atoms and two NO ligands were incorporated in the model. The occupancies of the atoms in the disordered ligands were refined with the constraint that the occupancies of atoms in one configuration were equal to one another and equal to 1 minus the occupancy of the atoms in the second configuration. Isotropic thermal parameters were refined with the constraint that the thermal parameter of an atom was equal to that of the corresponding atom in the second configuration.

(27) All least-squares refinements computed the agreement factors R and R_w according to $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w_i||F_o| - |F_c||^2/\sum w_i|F_o|^2]^{1/2}$, where F_o and F_c are the observed and calculated structure factors, respectively, and $w_i^{1/2} = 1/\sigma(F_o)$. The function minimized in all least-squares refinements was $\sum w_i||F_o| - |F_c||^2$.

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were assigned isotropic thermal parameters ($=CH_2$, $B = 7.0$; $-CH_3$, $B = 8.0$; solvate, $B = 15.0$). The rhenium, chlorine, phosphorus, fluorine, $=CH_2$ carbon, nitrogen, and oxygen atoms were refined with anisotropic thermal parameters. Other carbon atoms were refined with isotropic thermal parameters to give a R index of 0.060 with $R_w = 0.066$.[27] Since the phenyl rings had large thermal parameters, they were converted into rigid groups,[29] resulting in a drop, after several cycles of refinement, to a R index of 0.057 and R_w of 0.064. Next, the positions of the $=CH_2$ hydrogens were refined several times by using only the 1117 reflections for which $(\sin\theta)/\lambda \leq 0.35$[28] while parameters for all other atoms were kept constant. For the final cycle of refinement, only non-hydrogen atoms were refined, and a complete data set was used. The final R index was 0.058 with $R_w = 0.064$.

A stereoview of the molecular structure of **5** is given in Figure 2. Important bond distances and angles are summarized in Table III. It is clear that the $=CH_2$ moiety adopts the conformation approximated by Newman projection I (Figure 3). The computed angle of the Re–NO bond with the $=CH_2$ plane is ca. 3°.

Discussion

The route shown in Scheme I enables, for the first time, the preparation of an electrophilic $=CH_2$ complex both in quantity and analytically pure form. Three major factors likely contribute to the stability of **4** and **5**. First, third-row metals generally make stronger metal–ligand bonds than first- and second-row metals.[30] Second, there are no easily dissociable ligands in **4** and **5**. Third, **4** and **5** contain two good donor ligands that are also bulky: C_5Me_5[31] and PPh_3 or $P(OPh)_3$. These enhance the rhenium basicity and hence strengthen the $Re{=}CH_2$ π bond. The C_5Me_5 ligand also sterically inhibits the facile bimolecular decomposition pathway observed with $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(=CH_2)]^+PF_6^-$ (**3**).[18] Closely related $(\eta\text{-}C_5Me_5)Re(NO)(CO)(X)$ compounds have been studied by Graham.[22] He finds that the formyl complex $(\eta\text{-}C_5Me_5)Re(NO)(CO)(CHO)$ is stable as a solid to 69–70 °C, whereas the $\eta\text{-}C_5H_5$ homologue $(\eta\text{-}C_5H_5)Re(NO)(CO)(CHO)$[22,32,33] is only stable to −10 °C. Thus, the C_5Me_5 ligand also dramatically enhances stabilities in this series of rhenium complexes.

We have concentrated on defining properties of **4** and **5** that are unique to the $=CH_2$ ligand. The IR, NMR, and X-ray data all indicate that the $=CH_2$ carbon is approximately trigonal rather than "T-shaped" as in certain alkylidenes reported by Schrock.[11] All "T-shaped" alkylidenes contain a semibridging hydrogen and are characterized by anomalously low NMR $^1J_{^{13}C_\alpha-^1H_\alpha}$ (75–100 Hz) and IR ν_{C-H} (~2500 cm^{-1}).[34] Furthermore, they are found only on coordinatively unsaturated metals. The $^1J_{^{13}C_\alpha-^1H_\alpha}$ of ca. 150 Hz in **5** is in the range commonly found for essentially sp^2-hybridized carbons.[35]

The IR spectra in Figure 1 provide the first definitive determination of the stretching ν_{C-H} for a methylidene complex. The antisymmetric stretches[36,37] are split into doublets at 2987/2976 cm^{-1} and (ν_{C-D}) 2245/2238 cm^{-1}. The frequencies are somewhat lower than those in the organic homologue $(CH_3)_2C{=}CH_2$: 3085 (s) and 3019 (w) cm^{-1} (argon matrix, 20 K); 3076 (s) and 2986 (sh) cm^{-1} (liquid, −60 °C).[36] They are comparable to those found in the bridging methylidene complexes $(\eta\text{-}C_5H_5)(CO)_2Rh{-}CH_2{-}Rh(CO)_2(\eta\text{-}C_5H_5)$ (2963 (w) and 2903 (w) cm^{-1})[37a] and $Os_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$ (2990 (vw) and 2949 (w) cm^{-1}).[37b] Very recently, the stretching ν_{C-H} for CH_2 on Ru(001) have been assigned as 3050 (m) and 2940 (s) cm^{-1}.[37c]

The $=CH_2$ orientation depicted in Figures 2 and 3 agrees with that predicted by theory. Eisenstein has conducted Hückel MO calculations on the model fragment $[(\eta\text{-}C_5H_5)Re(NO)(PH_3)]^+$ and the methylidene complex, $[(\eta\text{-}C_5H_5)Re(NO)(PH_3)(=CH_2)]^+$.[23] The rhenium fragment HOMO was shown to be a d orbital that is coplanar with the Re–P bond and perpendicular to the Re–NO bond. The corresponding orbital for the $[(\eta\text{-}C_5Me_5)Re(NO)(PPh_3)]^+$ fragment is shown as II in Figure 3. Thus, the $=CH_2$ adopts a conformation that maximizes overlap of its vacant p orbital with the d-orbital HOMO. The LUMO in **4** and **5** is likely the $d\pi$–$p\pi$ $Re{=}CH_2$ antibonding combination.[23] However, the $d\pi$–$p\pi$ bonding combination would be predicted to drop sufficiently in energy to make a nonbonding rhenium d orbital (orthogonal to II and coplanar with the Re–NO bond)[38] the HOMO.

The $Re{=}CH_2$ bond length in **5**, 1.898 (18) Å, is close to the corresponding $Re{=}CHR$ bond length in the benzylidene complex, *ac*-$[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(=CHC_6H_5)]^+PF_6^-$, 1.949 (6) Å.[23] Several factors are likely to influence the relative lengths of these bonds. The $=CHC_6H_5$ ligand presents a somewhat greater steric demand than $=CH_2$, but the C_5Me_5 ligand is bulkier than C_5H_5. The C_5Me_5 ligand is a better donor than C_5H_5,[31] and this should make the $Re{=}CH_2$ π bond stronger and shorter. The latter factor probably dominates, since the Re–NO bond length in **5**, 1.696 (16) Å, appears shorter than the corresponding 1.761 (5) Å bond length in *ac*-$[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(=CHC_6H_5)]^+PF_6^-$. The long $Re{=}CH_2$ bond length noted for **4** in Table I is undoubtedly an artifact of the $NO/{=}CH_2$ disorder. Guggenberger and Schrock found a $Ta{=}CH_2$ bond length of 2.026 (10) Å in **2**.[11b]

One $Re{=}CH_2$ face of **5** is conspicuously shielded by a $P(OPh)_3$ phenyl ring (Figure 2). Hence it can be predicted that, as was shown with the benzylidene complex $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(=CHC_6H_5)]^+PF_6^-$,[23] nucleophiles will preferentially attack C_α from a direction anti to the phosphorus ligand.

The $Re{=}CH_2$ rotational barrier in $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(=CH_2)]^+PF_6^-$ (**3**) has been bounded as $\Delta G^\ddagger_{rot}$ (27 °C) > 15 kcal/mol.[19] On the basis of the steric and electronic factors described above, **4** and **5** are expected to have higher $Re{=}CH_2$ rotational barriers. We can bound $\Delta G^\ddagger_{rot}$ (~114 °C) for **4** and **5** as ≳19 kcal/mol, but unfortunately we cannot obtain precise values. Among other factors, negative $\Delta S^\ddagger$ can impede the observation of NMR coalescence phenomena. Rotational barriers determined to date for homologous compounds include (a) $\Delta H^\ddagger = 17.4 \pm 0.5$ kcal/mol and $\Delta S^\ddagger = -7.3 \pm 2.0$ eu for ethylidene *sc*-$[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(=CHCH_3)]^+PF_6^- \rightarrow$ *ac*-$[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(=CHCH_3)]^+PF_6^-$,[39] $\Delta H^\ddagger = 20.9 \pm 0.4$ kcal/mol and $\Delta S^\ddagger = -3.8 \pm 0.2$ eu for the corresponding *sc* → *ac* isomerization of the benzylidene complex, $[(\eta\text{-}C_5H_5)Re$-

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(29) Each phenyl group was refined with an enforced pseudo-D_{6h} symmetry, which differed from D_{6h} symmetry only in that the *ipso* carbon was not bound to a hydrogen atom. An additional parameter was refined for each group that varied carbon–carbon bond distances while maintaining pseudo-D_{6h} symmetry. See: Strouse, C. E. *Acta Crystallogr., Sect. A* **1970**, *A26*, 604. The model incorporated overall translational and librational movement as described by: Schomaker, V.; Trueblood, K. N. *Acta Crystallogr., Sect. B* **1968**, *B24*, 63. The elements of a translational matrix and the diagonal elements of a librational matrix were refined separately for each group; other matrix elements were held equal to zero.

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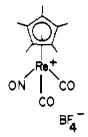
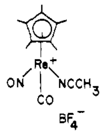
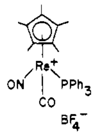
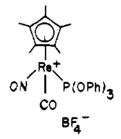
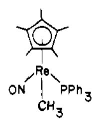
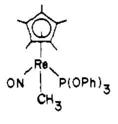
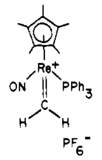
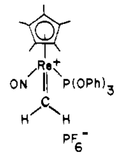
Table I. Spectroscopic Properties of New η-C_5Me_5 Rhenium Complexes

complex	^1H NMR,[a,b] δ	^{13}C NMR,[a] ppm	^{31}P NMR,[c] ppm	IR, cm^{-1}
 7	2.20 (s, C_5Me_5)[d]	187.1 (CO), 109.3 (C_3Me_5), 10.2 (C_5Me_5)[e]		$\nu_{C\equiv O}$ 2093 s, 2036 s, $\nu_{N\equiv O}$ 1986, s br[f]
 8	3.05 (s, $NCCH_3$), 2.27 (s, C_5Me_5)[e]	198.9 (CO), 139.3 (CH_3CN), 107.3 (C_5Me_5), 9.9 (C_5Me_5), 4.7 (CH_3CN)[e,g]		$\nu_{C\equiv O}$ 2015 s, $\nu_{N\equiv O}$ 1735 s[h]
 9a	7.6–7.3 (m, PPh_3), 1.94 (s, C_5Me_5)[h]	201.4 (CO), PPh_3 at 134.0 (d, $J_{^{13}C-^{31}P}$ = 12 Hz), 133.2 (s), 131.0 (d, J = 57 Hz) 130.5 (d, J = 12 Hz); 107.3 (C_5Me_5), 10.0 (C_5Me_5)[e]	13.9 (PPh_3)[e]	$\nu_{C\equiv O}$ 2002 s, $\nu_{N\equiv O}$ 1741 s[f]
 9b	7.6–7.3 (m, $P(OPh)_3$), 2.28 (s, C_5Me_5)[e]	$P(OPh)_3$ at 151.2 (d, $J_{^{13}C-^{31}P}$ = 8 Hz), 131.7 (s), 127.6 (s), 121.6 (s); 108.0 (C_5Me_5) 10.1 (C_5Me_5)[e]	116.0 ($P(OPh)_3$)[d]	$\nu_{C\equiv O}$ 2021 s, $\nu_{N\equiv O}$ 1755 s[f]
 10a	7.7–7.2 (m, PPh_3), 1.61 (s, C_5Me_5) 0.74 (d, $J_{^1H-^{31}P}$ = 6 Hz, Re-CH_3)[f]	PPh_3 at 137.4 (d, $J_{^{13}C-^{31}P}$ = 48 Hz), 134.8 (d, J = 11 Hz), 130.0 (s), 128.7 (d, J = 10 Hz); 98.4 (C_5Me_5), 9.7 (C_5Me_5), −22.4 (d, $J_{^{13}C-^{31}P}$ = 7 Hz, Re-CH_3)[i]	26.2 (PPh_3)[i]	$\nu_{N\equiv O}$ 1606 s[d]
 10b	7.3–7.0 (m, $P(OPh)_3$), 1.59 (s, C_5Me_5), 0.55 (d, $J_{^1H-^{31}P}$ = 6 Hz, Re-CH_3)[f,j]	$P(OPh)_3$ at 153.5 (d, $J_{^{13}C-^{31}P}$ = 9 Hz), 130.3 (s), 124.8 (s), 121.9 (d, J = 4 Hz); 100.4 (d, J = 2 Hz, C_5Me_5), 9.7 (C_5Me_5), −25.7 (d, $J_{^{13}C-^{31}P}$ = 11 Hz, Re-CH_3)[i]	116.8 ($P(OPh)_3$)[i]	$\nu_{N\equiv O}$ 1601 s[d]
 4	15.27 and 14.35 (two d, $J_{^1H_\alpha-^1H_{\alpha'}}$ = 6 Hz, $=CH_2$), 7.7–7.2 (m, PPh_3), 1.91 (s, C_5Me_5)[f]	287.7 (br s, $=CH_2$), PPh_3 at 133.9 (d, $J_{^{13}C-^{31}P}$ = 12 Hz), 133.6 (br s), 130.6 (d, J = 12 Hz), 129.9 (d, J = 59 Hz), 111.9 (C_5Me_5), 10.2 (C_5Me_5)[d]	23.7 (PPh_3)[f,k]	$\nu_{N\equiv O}$ 1708 s[d]
 5	14.49 and 14.14 (two d, $J_{^1H_\alpha-^1H_{\alpha'}}$ = 5 Hz, $=CH_2$), 7.5–7.0 (m, $P(OPh)_3$), 2.17 (s, C_5Me_5)[f]	293.3 (d, $J_{^{13}C-^{31}P}$ = 12 Hz, $=CH_2$), $P(OPh)_3$ at 150.4 (d, $J_{^{13}C-^{31}P}$ = 7 Hz), 131.2 (s), 127.4 (s), 120.5 (s); 111.3 (C_5Me_5), 10.4 (C_5Me_5)[f]	117.9 ($P(OPh)_3$)[f]	$\nu_{N\equiv O}$ 1726 s[d]

[a] Referenced to $(CH_3)_4Si$ internal standard. [b] 90–200 MHz. [c] Referenced to external 85% H_3PO_4. [d] $CDCl_3$. [e] Acetone-d_6. [f] CD_2Cl_2. [g] Gated decoupled spectrum shows q, $J_{^1H-^{13}C}$ = 130 Hz (C_5Me_5) and J = 139 Hz (CH_3CN). [h] CD_3CN. [i] C_6D_6. [j] In acetone-d_6, C_5Me_5 and Re–CH_3 resonances are at 1.68 and 0.71 δ. [k] PF_6^-: −144.5 ppm, septet, $J_{^{31}P-^{19}F}$ = 710 Hz.

$(NO)(PPh_3)(=CHC_6H_5)]^+PF_6^-$,[23] and (c) $\Delta H^\ddagger = 15.7 \pm 1.7$ kcal/mol and $\Delta S^\ddagger = -9.8 \pm 5.5$ eu for the *ac* → *sc* isomerization of the vinylidene, $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(=C=C(CH_3)C_6H_5)]^+SO_3F^-$.[40] In view of these data, we think it is unlikely that $\Delta G^\ddagger_{rot}$ for 4 and 5 are significantly above their boundary values. The $\Delta G^\ddagger_{rot}$ (100 °C) for $Ta=CH_2$ in 2 has been bounded as $\gtrsim 21.4$ kcal/mol.[11b]

The disorder of the small NO and $=CH_2$ ligands observed in the crystal structure of 4 has considerable precedent. Roper found the CO and $=CCl_2$ ligands in $Os(Cl)_2(PPh_3)_2(CO)(=CCl_2)$ to be disordered.[41] The μ-CH_2 and μ-CO are disordered in $Os_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$.[42] Such disorder would not be possible in crystals of optically pure **4**. Since **9a** can be resolved analogously to the C_5H_5 homologue,[25b,43] a more accurate crystal structure may prove possible. Speculatively, the tendency of crystals of **5** to crack upon cooling may be due to channels that are evident in the packing diagrams (Supplementary Material).

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Table II. Summary of Crystallographic Data for $[(\eta\text{-}C_5Me_5)Re(NO)(PPh_3)(=CH_2)]^+PF_6^-$ (4) and $[(\eta\text{-}C_5Me_5)Re(NO)(P(OPh)_3)(=CH_2)]^+PF_6^-\cdot CHCl_2CH_3$ ($5\cdot CHCl_2CH_3$)

	4	$5\cdot CHCl_2CH_3$
formula	$C_{29}H_{32}F_6NOP_2Re$	$C_{29}H_{32}F_6NO_4P_2Re\cdot C_2H_4Cl_2$
formula weight	772.7	919.7
cryst system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
cell dimens		
a, Å	11.127 (7)	8.666 (3)
b, Å	18.668 (9)	12.387 (5)
c, Å	14.497 (7)	34.90 (1)
β, deg	103.97 (4)	102.34 (3)
V, Å^3	2922 (2)	3360 (2)
Z	4	4
d_{obsd}, g cm^{-3}	1.70	1.69
d_{calcd}, g cm^{-3}	1.70	1.82
cryst dimens, mm	0.25 × 0.25 × 0.15	0.15 × 0.15 × 0.25
cryst faces	$00\bar{1}$, 001, $\bar{1}\bar{1}0$, $1\bar{1}0$, 010	100, $\bar{1}00$, 010, $0\bar{1}0$, 001, $00\bar{1}$
radiation, Å	λ(Mo Kα) = 0.71069	λ(Mo Kα) = 0.71069
temp of collection, °C	−160	25
data collection method	$\theta-2\theta$	$\theta-2\theta$
scan rate, deg min^{-1}	4.0	12.0
reflcns measd	$h,k,\pm l$	$h,k,\pm l$
scan range, deg	Kα_1 − 1.75 to Kα_2 + 1.5	Kα_1 − 0.75 to Kα_2 + 0.75
max 2θ, deg	45	50
no. of reflcns between std	97	97
total unique data	3789	5981
obsd data, $I > 3\sigma(I)$	2891	3038
abs coeff (μ), cm^{-1}	43.80	36.61
min transmission factor	0.684	0.729
mean transmission factor	0.732	0.758
max transmission factor	0.754	0.786
no. of variables	216	250
$R = \Sigma(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma\lvert F_o\rvert$	0.040	0.057
$R_w = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{1/2}$	0.049	0.064
goodness of fit	1.57	1.45
largest shift/error value on final cycle	0.15	0.24[a]

[a] Neglecting solvate.

Table III. Selected Bond Lengths (Å) and Angles (deg) in 4 and 5

atoms[a]	dist in 4	dist in 5
Re–C	2.145 (22) 2.152 (32)[b]	1.898 (18)
Re–N1	1.750 (14) 1.792 (19)[b]	1.696 (16)
Re–P1	2.423 (3)	2.363 (4)
Re–C11[c]	2.355 (11)	2.334 (14)
Re–C12	2.319 (11)	2.330 (14)
Re–C13	2.290 (10)	2.309 (16)
Re–C14	2.287 (10)	2.281 (16)
Re–C15	2.345 (10)	2.341 (15)
Re–C_5Me_5 Centroid	1.978	1.980
N1–O1	1.122 (19) 1.079 (24)[b]	1.212 (18)
C1–H1		0.886
C1–H2		0.995

atoms	angle in 4	angle in 5
C1–Re–N	101.6 (8) 100.0 (11)[b]	95.5 (7)
C1–Re–P	100.3 (6) 90.4 (8)[b]	91.9 (5)
N–Re–P	88.7 (5) 92.3 (6)[b]	93.3 (5)
Re–C1–H1		118
Re–C1–H2		138
H1–C1–H2		102
Re–N1–O1	177.5 (14) 171.2 (19)[b]	170.8 (15)

[a] Atoms in 4 are numbered analogously to those in 5 (Figure 2). [b] Disorder; see text. [c] C11–C15 are C_5Me_5 carbons.

Conclusion

Two stable electrophilic methylidene complexes, **4** and **5**, which are easy to prepare in quantity and in pure form, have been described. Spectroscopic features of the $=CH_2$ ligand have been examined in detail, and **5** has been characterized by an X-ray crystal structure. This work, and Schrock's data on $(\eta\text{-}C_5H_5)Ta(CH_3)(=CH_2)$ (**2**)[11] and $[W(PMe_3)_4(Cl)(=CH_2)]^+CF_3SO_3^-$,[16] provide important reference points for future studies of this increasingly available class of compounds. This work also establishes the needed foundation for the mechanistic study of the $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(=CH_2)]^+$ self-coupling described in the following paper.

Experimental Section

General. All reactions were done under an atmosphere of dry N_2. Acetone was commercial reagent grade unless specified otherwise. Acetonitrile was distilled from CaH_2. Dichloromethane, CD_2Cl_2, and $CDCl_2CDCl_2$ were distilled from P_2O_5. THF was distilled from sodium/benzophenone. Hexane, ether, and 2-butanone were used without purification. Commercial $CHCl_2CH_3$ (Aldrich) contained 3% dioxane, which was removed by sequential extraction with H_2O, concentrated H_2SO_4, and 2 × H_2O. The solvent was then dried overnight with P_2O_5, distilled, deoxygenated by purging with N_2, and stored in a N_2 atmosphere glovebox.

Pentamethylcyclopentadiene was prepared by the method of Threlkel and Bercaw.[44] $NO^+BF_4^-$ was purchased from Aldrich and stored under N_2. If colorless, it was used as received. Otherwise, it was washed with CH_2Cl_2 before use. Iodosobenzene diacetate was purchased from Aldrich or Eastman and converted to iodosobenzene by a literature procedure.[45] These compounds were stored in a refrigerator. PPh_3 was obtained from Aldrich or Pressure Chemical and was recrystallized from ethanol before use. $P(OPh)_3$ was obtained from Aldrich and used without purification. Solutions of $Li(C_2H_5)_3BH$, $Li(C_2H_5)_3BD$, $BH_3\cdot THF$, and $BD_3\cdot S(CH_3)_2$ were purchased from Aldrich and used without standardization. $Re_2(CO)_{10}$ was obtained from Pressure Chemical.

Commercial $Ph_3C^+PF_6^-$ (Aldrich or Columbia) gave erratic results unless purified. In a N_2 atmosphere glovebox, the salt was dissolved in a minimum of CH_2Cl_2 (ca. 5 mL/g), filtered through a medium porosity fritted glass funnel, and quickly precipitated with an equal volume of

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benzene. The resulting bright yellow powder was isolated by filtration, washed with benzene and hexane, and stored in a freezer under N_2.

Solution IR spectra were recorded on a Perkin-Elmer Model 521 spectrometer. FT IR were recorded on a Nicolet Model 7000 spectrometer with the assistance of Dr. Jim Liang. ^1H and ^{13}C NMR spectra were recorded at ambient probe temperature on Bruker WP-200 and JEOL FX90Q spectrometers and were referenced to internal $(CH_3)_4Si$. ^{31}P spectra were recorded on a Varian FT-80 spectrometer and were referenced to external 85% H_3PO_4. Mass spectra were obtained on an AEI-MS9 instrument. Melting points were determined on a Buchi Schmeltzpunktbestimmungsapparat and were not corrected. Microanalyses were conducted by Galbraith Laboratories.

Preparation of (η-C_5Me_5)Re(CO)$_3$ (6). A 100-mL round-bottom flask was charged with pentamethylcyclopentadiene (6.88 g, 50.5 mmol), $Re_2(CO)_{10}$ (10.0 g, 15.3 mmol), and a magnetic stir bar and was fitted with a reflux condenser and a N_2 inlet/oil bubbler. The flask was placed in a silicone oil bath on a stirrer/hot plate. *Caution! This reaction liberates CO and should be done in a good fume hood.* The reaction was stirred and heated. The $Re_2(CO)_{10}$ dissolved and at about 150 °C, gas began to evolve. The reaction was kept at 150 °C for 0.5 h and was then heated to 210 °C over the course of 2–5 h. The reaction was kept at 210 °C for 0.5 h. At this point, gas evolution had ceased. The heat was turned off and the flask was allowed to cool in the oil bath. Stirring was halted and by the time the flask reached room temperature, the contents had crystallized. Silica gel TLC showed that no $Re_2(CO)_{10}$ remained. The flask was chilled in the freezer, and the contents were transferred to a fritted glass Hirsch funnel and washed several times with cold hexane. Air was pulled through the product for several minutes to remove the hexane. This gave 6[21] as nearly colorless, very small plates (11.7 g, 29.0 mmol, 95%): 149–150 °C; ^1H NMR (δ, $CDCl_3$) δ 2.21 (s, 15 H); ^{13}C NMR (ppm, acetone-d_6) 199.1 (CO), 99.6 (C_5Me_5), 10.7 ($C_5\mathit{Me}_5$); IR (cm^{-1}, hexane) $\nu_{C\equiv O}$ 2015 s, 1915 s.

Preparation of [(η-C_5Me_5)Re(NO)(CO)$_2$]$^+BF_4^-$ (7). A Schlenk flask was charged with freshly degassed acetone (200 mL, distilled from anhydrous $CaSO_4$), 6 (7.34 g, 18.1 mmol), and a magnetic stir bar. The mixture was stirred under N_2 to dissolve the 6 and was then cooled to −78 °C. *Caution! This reaction liberates CO and should be done in a good fume hood.* Then $NO^+BF_4^-$ (3.29 g, 28.1 mmol) was added against a counterflow of N_2 gas. The solution immediately darkened and began to evolve gas. The reaction was stirred for 2 h at −78 °C, whereupon silica gel TLC showed that 6 had been consumed. The cold solution was poured directly into 1 L of ether in a large Erlenmeyer flask and swirled to give a yellow precipitate. The precipitate was separated by filtration, dissolved in CH_2Cl_2, filtered, and layered with ether. Crystals formed upon standing overnight in the freezer. Filtration gave 8.46 g (17.1 mmol, 95%) of 7 as yellow crystals, dec pt ca. 225 °C (gradual, without melting). Anal. Calcd for $C_{12}H_{15}BF_4NO_3Re$: C, 29.16; H, 3.06; N, 2.83. Found: C, 29.32; H, 3.32; N, 2.92.

Preparation of [(η-C_5Me_5)Re(NO)(CO)(NCCH$_3$)]$^+BF_4^-$ (8). In a typical reaction, a 250-mL Schlenk flask was charged with CH_3CN (150 mL), 7 (5.52 g, 11.17 mmol), and a magnetic stir bar. The resulting solution was cooled to 0 °C, and iodosobenzene (3.18 g, 14.45 mmol) was added. The reaction immediately began to turn orange-red and was stirred until all of the iodosobenzene had dissolved (0.5–3.0 h). A 2-mL aliquot was taken and worked up for ^1H NMR analysis (acetone-d_6). The δ 2.0 $C_5\mathit{Me}_5$ resonance of 7 was absent, and the δ 2.3 $C_5\mathit{Me}_5$ resonance of 8 was present. Had 7 remained, more iodosobenzene would have been added. Solvent was removed under aspirator vacuum at room temperature, and the resulting oil was layered with ether (100 mL). After 2 h, the oil had solidified. The solid was isolated by filtration, dissolved in a small amount of acetone, and layered with ether (200 mL). Small, powdery tan crystals of 8 formed upon standing overnight in the freezer. These were isolated by filtration and suction dried in air (5.26 g). Solvent was removed from the mother liquor and a second crop of crystals was similarly isolated (0.43 g). Thus obtained was 5.69 g (11.22 mmol, 91%) of 8, mp 153.5–154.5 °C.

Preparation of [(η-C_5Me_5)Re(NO)(PPh$_3$)(CO)]$^+BF_4^-$ (9a). A 250-mL round-bottom flask was charged with CH_3CN (100 mL), 7 (5.02 g, 10.15 mmol), and a magnetic stir bar and was fitted with a N_2 inlet/oil bubbler. The solution was cooled to 0 °C and iodosobenzene (2.48 g, 11.3 mmol) was added. Following ^1H NMR analysis as described above, another portion of iodosobenzene (0.75 g, 3.4 mmol) was added. The reaction was stirred for an additional 0.5 h and then the solvent was removed under aspirator vacuum at room temperature. Then PPh_3 (5.48 g, 20.9 mmol) and 2-butanone (100 mL) were added. The resulting mixture was refluxed for 9 h under N_2. Solvent was removed by rotary evaporation to give a dark brown oil that solidified as it cooled. This solid was transferred to a fritted glass funnel and was washed with several 20-mL portions of ether and then several small portions of THF. The resulting yellow-orange solid was dissolved in acetone, filtered, and then precipitated with ether. Very small yellow-orange crystals of 9a formed. These were isolated by filtration and washed with ether and THF (6.057 g, 8.31 mmol, 82%). The washes were collected and concentrated, and a second crop of 9a (0.221 g, 0.30 mmol, 3%) was similarly obtained from acetone/ether, mp 213–214 °C.

Preparation of [(η-C_5Me_5)Re(NO)(P(OPh)$_3$)(CO)]$^+BF_4^-$ (9b). A 300-mL round-bottom flask was charged with THF (175 mL), 8 (4.07 g, 8.03 mmol), and a magnetic stir bar. The flask was fitted with a reflux condenser and a N_2 inlet/oil bubbler. Then $P(OPh)_3$ (4.0 mL, 15 mmol) was added by syringe, and the mixture was refluxed for 14 h. The reaction was monitored by ^1H NMR as described in the preparation of 8. Solvent was removed from the reaction by rotary evaporation. The resulting yellow solid was transferred to a fritted glass funnel and was washed with ether and THF. It was then dissolved in a minimum of acetone and layered with ether (150 mL). Upon standing overnight in the freezer, large yellow crystals of 9b formed. These were isolated by filtration and air-dried (4.49 g, 5.78 mmol, 72%). Solvent was removed from the mother liquor, and a second crop of 9b was similarly obtained from acetone/ether (0.22 g, 0.28 mmol, 4%). Mp 173.5–174.5 °C.

Preparation of (η-C_5Me_5)Re(NO)(PPh$_3$)(CH$_3$) (10a). A 100-mL Schlenk flask was charged with THF (50 mL), 9a (5.00 g, 7.95 mmol), and a magnetic stir bar. The flask was capped with a rubber septum, and 16 mL of 1.0 M $Li(C_2H_5)_3BH$ in THF (16 mmol) was injected. Carbonyl 9a immediately dissolved and a honey-brown solution formed. Then 30 mL of 1.0 M $BH_3{\cdot}THF$ (30 mmol) was injected. The solution turned reddish brown. After 0.5 h, solvent was removed under oil pump vacuum. The flask was transferred to a N_2 atmosphere glovebox and the red-brown residue was extracted with benzene. The extract was passed through a 2.5-cm silica gel column and concentrated by rotary evaporation to a red-orange powder (3.67 g, 5.84 mmol, 73%). Red needles of 10a were obtained by layering a THF solution with hexane; this sample was used for analytical data: mp 133–135 °C dec; mass spectrum (16 eV, 180 °C inlet), *m/e* 629 (M^+, ^{187}Re, 100%), 614 ($M^+ - CH_3$, 11%), 351 (M^+ − $OPPh_3$, 7%), 262 ($^+PPh_3$, 35%). Anal. Calcd for $C_{29}H_{33}NOPRe$: C, 55.40; H, 5.29; N, 2.23; P, 4.93. Found: C, 55.27; H, 5.40; N, 2.49; P, 4.92.

Preparation of (η-C_5Me_5)Re(NO)(P(OPh)$_3$)(CH$_3$) (10b). In a N_2 atmosphere glovebox, a 250-mL round-bottom flask was charged with THF (100 mL), 9b (4.30 g, 5.54 mmol), and a magnetic stir bar. Then $NaBH_4$ (0.42 g, 8.6 mmol) was added. The reaction was stoppered tightly and stirred overnight to give a red solution. Solvent was then removed by rotary evaporation, and the resulting residue was extracted with benzene. The extract was passed through a 3-cm silica gel column and concentrated to a red residue by rotary evaporation under a oil pump vacuum. The residue was dissolved in a minimum of ether and hexane (150 mL) was added. The solution was concentrated by rotary evaporation, whereupon bright red crystals of 10b formed. These were collected by filtration (2.41 g, 3.56 mmol, 64%): mp 135–136 °C; mass spectrum (16 eV, 230 °C inlet), *m/e* 677 (M^+, ^{187}Re, 100%), 351 (M^+ − $OP(OPh)_3$, 46%), 310 ($^+P(OPh)_3$, 15%), 217 ($^+P(OPh)_2$, 64%).

Preparation of [(η-C_5Me_5)Re(NO)(PPh$_3$)(=CH$_2$)]$^+PF_6^-$ (4). In a N_2 atmosphere glovebox, a 100-mL Schlenk flask was charged with $CHCl_2CH_3$ (30 mL), 10a (0.165 g, 0.262 mmol), and a magnetic stir bar. The flask was capped with a rubber septum, removed from the box, attached to a N_2 line, and cooled to −78 °C. The septum was removed and $Ph_3C^+PF_6^-$ (0.102 g, 0.262 mmol) was added against a N_2 flow. The reaction was stirred at −78 °C for 2.5 h, whereupon hexane (60 mL) was slowly layered onto the reaction mixture by means of a cannula. The flask was transferred to a −15 °C freezer and allowed to stand for 2 days. Brown prisms of 4 formed. These were collected by filtration and washed with small amounts of hexane and benzene (0.142 g, 1.84 mmol, 70%), mp 130–140 °C dec. Anal. Calcd for $C_{29}H_{32}F_6NOP_2Re$: C, 45.10; H, 4.18; N, 1.81; P, 8.02. Found: C, 44.85; H, 4.33; N, 1.75; P, 7.87.

Preparation of [(η-C_5Me_5)Re(NO)(P(OPh)$_3$)(=CH$_2$)]$^+PF_6^-\cdot$CHCl$_2$CH$_3$ (5·CHCl$_2$CH$_3$). In a N_2 atmosphere glovebox, a 100-mL Schlenk flask was charged with $CHCl_2CH_3$ (7 mL), 10b (0.111 g, 0.164 mmol), and a stir bar. The flask was stoppered, removed from the box, attached to a N_2 line, and cooled to −78 °C. Solid $Ph_3C^+PF_6^-$ (0.064 g, 0.165 mmol) was added against a stream of N_2 gas. The reaction was stirred at a low temperature for 2 h, removed from the cold bath, and immediately connected to a high vacuum pump. The solvent was completely removed and the flask was returned to the glovebox. Benzene (3 mL) was added to the residue, yielding a suspension. Crude product was isolated by filtration, washed with small portions of benzene and hexane, and recrystallized from $CHCl_2CH_3$/hexane. Thus, obtained was 0.121 g (0.130 mmol, 78%) of 5· $CHCl_2CH_3$, dec pt ca. 115 °C (gradual, without melting).

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Registry No. **4**, 86497-25-8; **5**·$CHCl_2CH_3$, 86497-28-1; **6**, 12130-88-0; **7**, 86497-29-2; **8**, 86507-83-7; **9a**, 86497-31-6; **9b**, 86497-33-8; **10a**, 86497-34-9; **10b**, 86497-35-0; $Re_2(CO)_{10}$, 14285-68-8; $NO^+BF_4^-$, 14635-75-7; $Li(C_2H_5)_3BH$, 22560-16-3; $NaBH_4$, 16940-66-2; $Ph_3C^+PF_6^-$, 437-17-2; $C_6H_5I^+{-}O^-$, 536-80-1.

Supplementary Material Available: Tables of bond distances and angles, atomic coordinates, thermal parameters, and structure factors for **4** and **5**·$CHCl_2CH_3$, and figures showing atom numbering and crystal packing (47 pages). Ordering information is given on any current masthead page.

Mechanism of Coupling of $=CH_2$ to $H_2C{=}CH_2$ at a Homogeneous $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)^+$ Center. Remarkable Enantiomer Self-Recognition

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Abstract: The methylidene complex $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)({=}CH_2)]^+PF_6^-$ (**1**) couples to the ethylene complex $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CH_2)]^+PF_6^-$ (**2**; ca. 50%) at 273–308 K in CH_2Cl_2. The byproduct $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)_2]^+PF_6^-$ (**3**; ca. 25%) or, in the presence of CH_3CN, $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(NCCH_3)]^+PF_6^-$ (**5**; ca. 50%) also forms. The rate of coupling is second order in **1** and not affected by the presence of 5–10 equiv of RCN. Data collected from 273 to 308 K give $\Delta H^{\ddagger} = 9.8 \pm 0.6$ kcal/mol and $\Delta S^{\ddagger} = -33.8 \pm 1.0$ eu. At 298 K, $k_{=CH_2}/k_{=CD_2} = 0.39 \pm 0.03$. Surprisingly, optically pure **1** couples 2.3 times faster than racemic **1**. Crossover experiments show that no PPh_3 dissociation or intermolecular $=CH_2$ scrambling occurs prior to the rate-determining coupling step, *and that the RR and SS transition states are greatly preferred over the RS transition state* (enantiomer self-recognition). Experiments with optically pure **1** show that **2** is formed with >98% *retention* at rhenium. An X-ray crystal structure of (+)-(*SS*)-$[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(NCCH(C_6H_5)CH_2CH_3)]^+PF_6^-$ ((+)-(*SS*)-**6**) shows that RCN adducts also form with retention. These data are interpreted as evidence for the rate-determining formation of initial $\overline{ReCH_2Re}CH_2$ (**7a**) or $ReCH_2CH_2Re$ (**7b**) intermediates. Subsequent rapid conversion to primary monomeric products **2** and $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(S)]^+PF_6^-$ (**8**; S = CH_2Cl_2 or vacant coordination site) is proposed. Comparisons are made to other homogeneous and heterogeneous $=CH_2$ coupling reactions.

Metal-bound methylidenes ($=CH_2$) play key roles in homogeneous catalytic reactions such as olefin metathesis,[3] olefin cyclopropanation,[4] and the heterogeneous Fischer–Tropsch process.[5] Hence their chemistry—and in particular carbon–carbon bond-forming reactions—has been of intense interest.[5-11]

In a recent study, Pettit demonstrated that surface-bound $=CH_2$ rapidly dimerizes to $H_2C{=}CH_2$ in the absence of hydrogen.[5e,f] Curiously, attempts to generate *homogeneous* $L_nM{=}CH_2$ complexes have often given $L_nM(H_2C{=}CH_2)$ complexes in ca. 50% yields.[7b,10,11] Schrock's isolable *nucleophilic* methylidene complex $(\eta\text{-}C_5H_5)_2Ta(CH_3)({=}CH_2)$[6a,b] decomposes to the ethylene complex $(\eta\text{-}C_5H_5)_2Ta(CH_3)(H_2C{=}CH_2)$.[6b] We have sought to explore the generality and better understand the mechanisms of such ethylene-forming reactions.

In the preceding paper,[8d] we described the synthesis and structural characterization of electrophilic C_5Me_5 methylidene complexes, $[(\eta\text{-}C_5Me_5)Re(NO)(L)({=}CH_2)]^+PF_6^-$ (L = PPh_3, $P(OPh)_3$), which are stable as solids to >100 °C. In this paper, we examine the decomposition chemistry of the much more reactive C_5H_5 methylidene $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)({=}CH_2)]^+PF_6^-$ (**1**),[8a,b] which is readily available in optically pure form.[8c] We report herein that **1** undergoes smooth ambient temperature coupling to the ethylene complex $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CH_2)]^+PF_6^-$ (**2**) and present stereochemical and kinetic data that we interpret as evidence for $\overline{ReCH_2Re}CH_2$ and/or $ReCH_2CH_2Re$ intermediates. Furthermore, this transformation exhibits a remarkable degree of enantiomer self-rec-

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