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Synthesis and reactivity of bridging bis(alkyl) and bis(alkylidene) complexes derived from the chiral rhenium fragment $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$

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Abstract

Reactions of $Li^+[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^-$ and $TfO(CH_2)_nOTf$ (0.5 equiv.; **a**, $n = 3$; **b**, $n = 4$; **c**, $n = 5$; **d**, $n = 8$) give the bridging bis(alkyl) complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2)_n(PPh_3)(NO)Re(\eta^5\text{-}C_5H_5)$ (**7a–d**, 80–89%) as 50–75:50–25 mixtures of configurational diastereomers (*meso, dl*). Reactions of **7** and $Ph_3C^+PF_6^-$ (2 equiv.) give the bridging bis(alkylidene) complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}CH(CH_2)_{n-2}HC{=})(PPh_3)(NO)Re(\eta^5\text{-}C_5H_5)]^{2+}2PF_6^-$ (**3a–d**, 76–93%). When heated in chlorobenzene, **3c** and **3d** rearrange ($k_{obs} = 3.9 \times 10^{-5}$ s^{-1}, **3c**, 72°C; 6.3×10^{-5} s^{-1}, **3d**, 66°C) to the bridging bis(alkene) complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CH(CH_2)_{n-4}HC{=}CH_2)(PPh_3)(NO)Re(\eta^5\text{-}C_5H_5)]^{2+}2PF_6^-$ (**5c,d**$^{2+}$ $2PF_6^-$, 90–97%). No cycloalkene complexes derived from Re=CHR/Re=CHR coupling are detected. Complexes **5c**$^{2+}$ $2BF_4^-$ and **5d**$^{2+}$ $2BF_4^-$ are independently prepared by reactions of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$, $HBF_4 \cdot OEt_2$, and α,ω-dienes in chlorobenzene.

There has been considerable interest in the synthesis, structure, and reactivity of transition metal complexes of the general formula **A**, which contain an unsupported polymethylene chain spanning two metals [1,2]. Such compounds have attracted attention as models for intermediates in a variety of catalytic reactions [1,3]. In contrast, analogous bis(alkylidene) complexes **B**, which contain a carbene-tethered methylene chain, have not to our knowledge been previously reported. However, in important recent work, Macomber has prepared a series of related neutral Group VI Fischer carbene complexes [4]. Significantly, bis(alkylidene) complexes **B** have also been proposed as intermediates in catalytic processes, particularly in pretroleum feedstock chemistry [5].

$L_xM{-}(CH_2)_n{-}ML_x$

A

$[L_xM{=}CH{-}(CH_2)_{n-2}{-}HC{=}ML_x]^{z+}$

B

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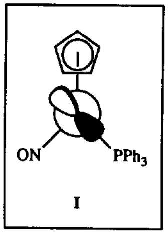
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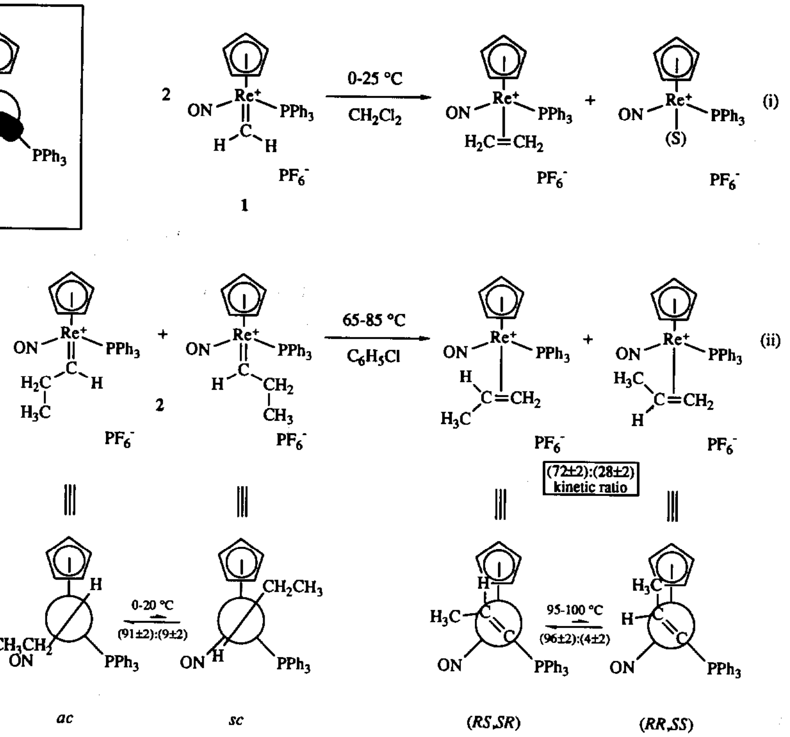
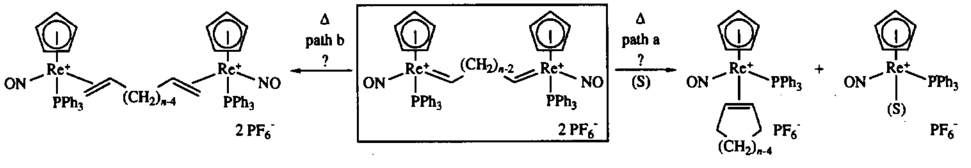


Scheme 1. Comparison of the thermolysis of the methylidene complex **1** (eq. i) and propylidene complex **2** (eq. ii), and structures of isomeric reactants and products.

We have had an ongoing interest in the physical and chemical properties of chiral rhenium alkylidene complexes of the formula $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CHR)]^+X^-$ [6–9]. In particular, we have conducted detailed mechanistic studies of their thermal reactions [7,9]. For example, the methylidene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CH_2)]^+PF_6^-$ (**1**) undergoes bimolecular coupling at 0–25°C to the ethylene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C=CH_2)]^+PF_6^-$, as shown in eq. i of Scheme 1 [7]. However, the propylidene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CH_2CH_2CH_3)]^+PF_6^-$ (**2**) is more stable, and instead undergoes a unimolecular 1,2-hydride shift at 65–85°C to give the propene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C=CHCH_3)]^+PF_6^-$, as shown in eq. ii of Scheme 1 [9].

We wondered which of two preceding thermolysis pathways would dominate with the analogous bridging bis(alkylidene) complexes, $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CH(CH_2)_{n-2}HC=)(PPh_3)(NO)Re(\eta^5\text{-}C_5H_5)]^{2+}2PF_6^-$ (**3**). As depicted in Scheme 2, either intramolecular coupling to give the corresponding cycloalkene complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\overline{CH=CH(CH_2)_{n-2}})]^+PF_6^-$ ($\mathbf{4}^+PF_6^-$), or hydride shifts to yield bridging bis(alkene) complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C=CH(CH_2)_{n-4}CH=CH_2)(PPh_3)(NO)Re(\eta^5\text{-}C_5H_5)]^{2+}2PF_6^-$ ($\mathbf{5}^{2+}2PF_6^-$), could in principle occur. Authentic samples of the potential cycloalkene products $\mathbf{4}^+X^-$ have recently been prepared in connection with another project [8]. Thus, we set out to synthesize a series of bis(alkylidene) complexes **3**, and examine their thermal behavior. Our findings are reported here.



$5^{2+}2PF_6^-$ 3 $4^+PF_6^-$

Scheme 2. Possible thermolysis pathways for the bis(alkylidene) complexes **3**.

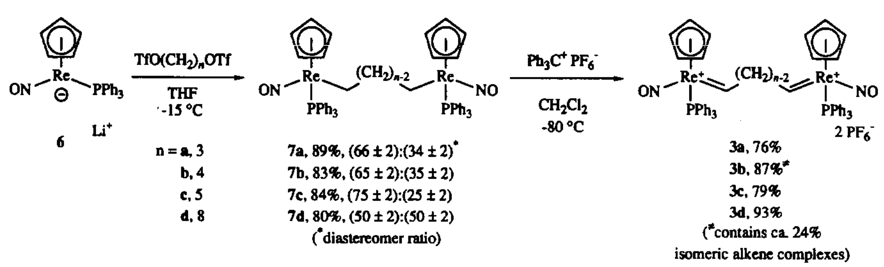
The data that follow are more readily assimilated if prefaced by a summary of previously established bonding properties. First, the rhenium fragment $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ (**I**) possesses the high-lying *d*-orbital HOMO shown in Scheme 1 [10]. Accordingly, alkylidene and alkene ligands adopt conformations that maximize overlap of their acceptor orbitals with this donor orbital. Furthermore, alkylidene complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}CHR)]^+X^-$ can exhibit two Re=C geometric isomers, *anticlinal* (*ac*) and *synclinal* (*sc*), as illustrated for **2** in Scheme 1 [6]. The former, which has the alkyl substituent *syn* to the small nitrosyl ligand, is more stable ($K_{eq} = 9\text{–}10$), and interconversion occurs readily at room temperature ($\Delta H^\ddagger$ ($sc \rightarrow ac$) = 18–21 kcal/mol). Isomers of monosubstituted alkene complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHR)]^+X^-$ have been analyzed in detail elsewhere [11]. As shown in Scheme 1 for $R = CH_3$, two π configurational diastereomers are possible, (*RS*,*SR*) and (*RR*,*SS*). These differ in the alkene enantioface bound to rhenium. The former, which has the alkyl substituent directed towards the nitrosyl ligand, is more stable ($K_{eq} = 20\text{–}30$). However, temperatures of 95–100°C are required to establish equilibrium.

Results

Synthesis of bis(alkyl) complexes

The nucleophilic rhenium anion, $Li^+[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^-$ (**6**), was generated in THF at −15°C as previously described [12], and treated with 0.5 equiv. of the bis(triflates) $TfO(CH_2)_nOTf$ [13] as shown in Scheme 3 (**a**, $n = 3$; **b**, $n = 4$; **c**, $n = 5$; **d**, $n = 8$). Workup gave the bridging (bis)alkyl complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2)_n(PPh_3)(NO)Re(\eta^5\text{-}C_5H_5)$ (**7a–d**) as yellow-orange powders in 80–89% yields. Correct microanalyses were obtained for **7a**,**b**,**d**. Exploratory NMR experiments showed that **7b–d** could be similarly accessed from the bis(iodides) $I(CH_2)_nI$. However, in the case of **7a**, the iodide complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(I)$ [14] also formed, and could not be easily separated from the product.

Complexes **7a–d** were characterized by IR and NMR (^1H, ^{13}C, ^{31}P) spectroscopy, as summarized in the Experimental section. They were obtained as 50–75 : 50–25 mixtures of *meso* and *dl* configurational diastereomers (Scheme 3), as assayed by integration of the cyclopentadienyl ^1H NMR resonances. The diastereomers were inseparable by column and thin layer chromatography, although some resolution was achieved by analytical scale silica gel HPLC. They also generally gave distinct PPh_3 ^{31}P NMR and methylene ^{13}C NMR resonances, but the methylene ^1H NMR resonances overlapped in all cases. Otherwise, properties resembled those reported previously for the simple monomeric alkyl complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2R)$ [6a,b].



Scheme 3. Synthesis of bridging bis(alkyl) and bis(alkylidene) complexes.

Synthesis of bis(alkylidene) complexes

Unbranched alkyl complexes (η^5-C_5H_5)Re(NO)(PPh_3)(CH_2R) have previously been shown to undergo predominant α-hydride abstraction when treated with the trityl cation, $Ph_3C^+X^-$ [6a,b; 9]. Thus, the bis(alkyl) complexes **7a–d** and $Ph_3C^+PF_6^-$ (2.0–2.1 equiv.) were allowed to react in CH_2Cl_2 at −80°C, as shown in Scheme 3. Workup gave the bridging bis(alkylidene) complexes [(η^5-C_5H_5)Re(NO)(PPh_3)(=$CH(CH_2)_{n-2}HC$=)(PPh_3)(NO)Re(η^5-C_5H_5)]$^{2+}2PF_6^-$ (**3a–d**) as air-stable tan powders in 76–93% yields. Complexes **3a,b,d** gave correct microanalyses.

Complexes **3a–d** exhibited IR ν(NO) values (Experimental section) that were similar to those previously reported for the monomers [(η^5-C_5H_5)Re(NO)(PPh_3)(=CHR)]$^+X^-$ [6–8]. However, they were only sparingly soluble in acetone and dichloromethane, and ^{13}C NMR spectra could not be obtained under conditions analogous to those used for **7**. Thus, NMR spectra of **3b–d** were recorded in the more polar solvent nitromethane-d_3. Characteristic [6–8] downfield =CHR ^{13}C NMR (309–313 ppm) and ^1H NMR (δ 15.5–16.2) resonances were observed. The ^{31}P NMR spectra showed PPh_3 ligand resonances at 18–20 ppm.

The NMR spectra also showed that **3** exist as complex mixtures of isomers. Based upon the analysis given above for propylidene complex **2** (Scheme 1), each configurational diastereomer of **3** (*meso, dl*) should exist as a *ca.* 81 : 18 : 1 mixture of *ac/ac*, *ac/sc*, and *sc/sc* Re=C geometric isomers. Only assignments of resonances of the major *ac/ac* isomers were generally attempted (Experimental section). In the cases of **3c,d**, no evidence was observed for isomeric β-hydride elimination products such as mixed alkylidene/alkene complexes or the bis(alkene) complexes **5c,d**$^{2+}2PF_6^-$ (Schemes 2, 4). These would exhibit ^{31}P NMR chemical shifts in the region characteristic of monosubstituted alkene complexes [(η^5-C_5H_5)Re(NO)(PPh_3)(H_2C=CHR)]$^+X^-$ (9–11 ppm) [11]. However, **3b** contained *ca.* 24% of isomeric alkene complexes.

Synthesis of bis(alkene) complexes

A chlorobenzene solution of **3c** was kept at 72°C and monitored by ^{31}P NMR spectroscopy. The resonances of **3c** diminished as a set of very closely overlapping peaks appeared (11.0 ppm). As is shown in Fig. 1, first-order rate law was followed through $> 2t_{1/2}$, with $k_{obs} = (3.89 \pm 0.06) \times 10^{-5}$ s^{-1}. The chemical shift of the product was similar to those of analogous monomeric monosubstituted alkene complexes, and distinct from that of the previously reported cyclopentene complex [(η^5-C_5H_5)Re(NO)(PPh_3)($\overline{HC{=}CH(CH_2)_3}$)]$^+BF_4^-$ (**4c**$^+BF_4^-$, 8.2 ppm, 82°C,

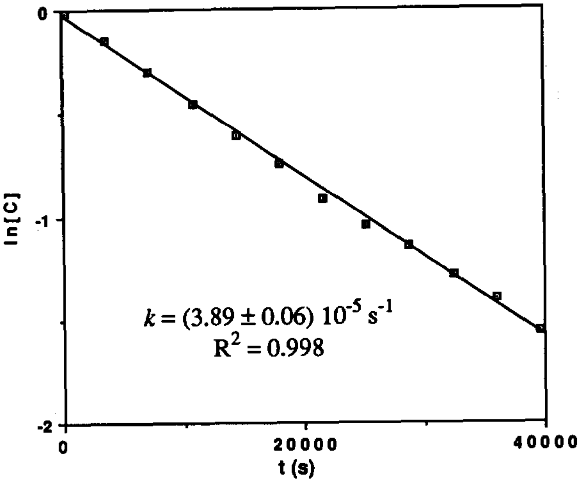
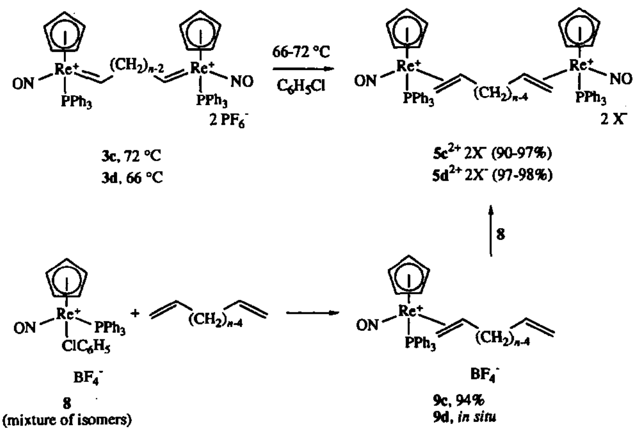


Fig. 1. Plot of ln[C] *vs*. time for the conversion of **3c** to $\mathbf{5c}^{2+}$ $2PF_6^-$ in chlorobenzene at 72°C (through 79% completion).

C_6H_5Cl, 9.2 ppm, $CDCl_3$) [7,9]. Complex $\mathbf{4c}^+BF_4^-$ is stable in chlorobenzene at 100°C [9].

Complex **3d** analogously converted to a new compound in chlorobenzene at 66°C (10.5 ppm). The rate ($k_{obs} = (6.3 \pm 0.2) \times 10^{-5}\ s^{-1}$) was faster than that of **3c**, despite the lower temperature. An analytically pure product was isolated from a preparative reaction in 97% yield. The ^{31}P NMR chemical shift (10.9, 11.0 ppm, $CDCl_3$) differed from that found for the cyclooctene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\overline{HC{=}CH(CH_2)_6})]^+BF_4^-$ ($\mathbf{4d}^+BF_4^-$, 9.0 ppm, $CDCl_3$) [7].

Hence, the thermolysis products were assigned as the bridging bis(alkene) complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CH(CH_2)_{n-4}HC{=}CH_2)(PPh_3)(NO)\text{-}Re(\eta^5\text{-}C_5H_5)]^{2+}2PF_6^-$ ($\mathbf{5c,d}^{2+}2PF_6^-$; Scheme 4). However, based upon the data for propylidene complex **2** (Scheme 1), *ca*. 72:28 mixtures of π configurational



Scheme 4. Synthesis of bis(alkene) complexes $\mathbf{5c,d}^{2+}$ $2X^-$.

diastereomers ((*RS,SR*) and (*RR,SS*)) would be expected at each rhenium center. Such diastereomers often give identical ^{31}P NMR chemical shifts, but most ^{1}H and ^{13}C NMR resonances are distinct [11]. Thus, in order to simplify NMR characterization, we sought to conduct independent syntheses of $\mathbf{5c}^{2+}2X^-$ and $\mathbf{5d}^{2+}2X^-$ utilizing reaction temperatures of *ca.* 100°C. As noted above, these should give $\geq 95:5$ mixtures of diastereomers at each rhenium center. In the absence of any chiral recognition phenomena, ca. 45:45:5:5 mixtures of (*RS,SR*)/(*RS,SR*) (*dl*), (*RS,SR*)/(*SR,RS*) (*meso*), (*RS,SR*)/(*RR,SS*), and (*RS,SR*)/(*SS,RR*) isomers would be obtained.

Thus, the substitution-labile chlorobenzene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClC_6H_5)]^+BF_4^-$ (**8**), which is a mixture of linkage and other isomers, was generated at −45°C as previously described [15]. Excess 1,4-pentadiene was added, and the sample was kept at 100°C for 36 h. Workup gave the 1:1 complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHCH_2CH{=}CH_2)]^+BF_4^-$ (**9c**) in 94% yield as a $(98 \pm 2):(2 \pm 2)$ mixture of (*RS,SR*)/(*RR,SS*) diastereomers (Scheme 4). Complex **9c** was characterized by microanalysis, and by IR and NMR (^{1}H, ^{13}C, ^{31}P) spectroscopy, as described in the experimental section.

Next, **8** was similarly allowed to react with an equimolar amount of **9c** (Scheme 4). Workup gave the bis(alkene) complex $\mathbf{5c}^{2+}2BF_4^-$ in 97% yield. Two diastereomers greatly predominated ($(56 \pm 2):(44 \pm 2)$), and the mixture was characterized analogously to **9c**. The ^{1}H, ^{13}C, and ^{31}P NMR chemical shifts closely matched those of major diastereomers of $\mathbf{5c}^{2+}2PF_6^-$ obtained from the thermolysis of **3c** (Experimental section). However, additional minor diastereomers were evident in the thermolysis samples. Finally, **8** was analogously reacted with 0.5 equiv. of 1,7-octadiene. Workup gave the 2:1 complex $\mathbf{5d}^{2+}2BF_4^-$ in 98% yield as a *ca.* 37:35:13:15 mixture of diastereomers. The NMR properties were very similar to those of the $\mathbf{5d}^{2+}2PF_6^-$ obtained from **3d**.

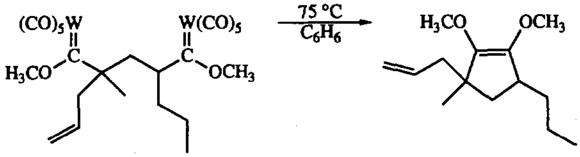
Discussion

Other investigators have previously reported the synthesis of bridging bis(alkyl) complexes **A** from transition metal anions and bis(triflates) or bis(iodides) [1, 2c,d,e,i]. However, the metal endgroups have in all cases been achiral. A few bridging bis(alkyl) complexes with chiral endgroups have been prepared, but always by modification of an existing complex **A** [16]. Also, chiral bridging bis(acyl) complexes have been synthesized by reactions of phosphines and complexes **A** that contain carbonyl ligands [2i,16]. Diastereoselectivities are in all instances modest, paralleling our results with rhenium complexes **7**.

The chirality of the rhenium fragment **I** often provides a valuable probe of mechanism and dynamic processes. However, the resulting capability for configurational diastereomers in dirhenium complexes such as **3**, $\mathbf{5}^{2+}2X^-$, and **7** is, for the purposes of this study, a complication. This issue can in principle, be circumvented by syntheses starting with enantiomerically pure monorhenium compounds. Unfortunately, the key intermediate in Scheme 3, $Li^+[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^-$ (**6**), is (if chiral) configurationally unstable [12]. However, alternative routes that would avoid this problem can be envisioned. For example, the acyl complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(COR)$ are easily obtained in enantiomerically pure form, and are reduced by $BH_3 \cdot THF$ to alkyl complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2R)$

with retention of configuration at rhenium [6d,17]. Also, deprotonation/protonation sequences that convert alkene complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHR)]^+X^-$ to alkylidene complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}CHCH_2R)]^+X^-$ are now available [6e,8].

Despite the various possibilities for isomers, an unequivocal answer to the question posed in Scheme 2 has been realized. Namely, upon thermolysis, the termini of bis(alkylidene) complexes **3c,d** undergo independent 1,2-hydride shifts to give bis(alkene) complexes $\mathbf{5c}^{2+}2PF_6^-$ and $\mathbf{5d}^{2+}2PF_6^-$. The proximity of the two alkylidene centers is not sufficient to effect the type of coupling process observed with the methylidene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}CH_2)]^+PF_6^-$ (**1**; Scheme 1, eq. i). However, in striking contrast, Macomber has reported that the tungsten Fischer bis(carbene) complex **10** shown in eq. iii undergoes thermolysis to a cycloalkene in high yield [4a]. This difference may be due to the availability of coupling pathways initiated by CO dissociation from **10**, and/or the fact that only a single C_β hydrogen atom is present. Monomeric Group VI Fischer carbene complexes frequently give coupled alkenes when heated [18], and few simple alkene complexes of $(CO)_5M$ fragments appear to be known.



(iii)

10

90%

The rate of rearrangement of propylidene complex **2** has been measured in chlorobenzene at a variety of temperatures ($k_{obs} = 4.3 \times 10^{-5}$, 65°C; 2.0×10^{-4}, 73°C) [9]. These data establish the reactivity order **3d** > **2** > **3c**. The rate difference between **3d** and **2** (65–66°C) is small, but that between **2** and **3c** (72–73°C) is a factor of five. We have previously shown that 1,2-hydride migrations in monomeric alkylidene complexes are accelerated by (a) an increase in electrophilicity at C_α, and (b) electron releasing or carbocation-stabilizing substituents at C_β. The Re=C bond in **3** and monomeric analogs is highly polarized, with substantial positive charge on carbon as evidenced by reactions with nucleophiles [6]. Thus, one Re=C terminus of **3c** likely exerts an inductive electron withdrawing effect upon C_β of the other terminus. An incipient carbocation would be destabilized, rationalizing the slower rate of rearrangement of **3c**. Also, any Re=C inductive effect would be greatly attenuated or absent in **3d**, consistent with the faster rate. Conceivably, conformational properties of the methylene chains of **3c,d** might also affect their relative reactivities.

No mixed alkylidene/alkene intermediates were detected during the thermolysis of **3c,d**. However, many of the NMR resonances of such species should overlap with those of the reactants and products. Analysis is further complicated by the numerous reactant and product isomers. Nonetheless, no hystereses or other evidence for non-steady-state intermediates were observed in the first-order rate plots.

Finally, the mechanism of hydride abstraction from monomeric alkyl complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2R)$ by $Ph_3C^+X^-$ has been studied in considerable detail [19]. An initial electron transfer from rhenium to Ph_3C^+, followed by a subsequent hydrogen atom transfer, has been established. Thus, if the termini of bis(alkyl) complexes **7** were to react in sequence by an analogous stepwise process, radical cation intermediates of the formulae **C** and **D** would form. Several irreversible intramolecular reactions of **C** and **D** can be readily envisioned. However, as with the thermolysis of **3c,d**, the termini appear to react independently.

$$\underset{\mathbf{C}}{[\mathrm{Re}]\text{—}\mathrm{CH_2}\text{—}(\mathrm{CH_2})_{n\text{-}2}\text{—}\mathrm{CH_2}\text{—}[\mathrm{Re}]^{+\bullet}} \qquad \underset{\mathbf{D}}{[\mathrm{Re}]^{+\bullet}\text{—}\mathrm{CH_2}\text{—}(\mathrm{CH_2})_{n\text{-}2}\text{—}\mathrm{CH}\text{=}[\mathrm{Re}]^{+}}$$

$$[\mathrm{Re}] = (\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Re(NO)(PPh_3)}$$

In summary, the above data, together with previous studies abstracted in Scheme 1 [7,9], provide a detailed and comprehensive picture of the thermal chemistry of alkylidene complexes of the rhenium fragment $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$. Although this concludes our present plans for work in this area, investigations of related thermal processes involving vinylidene complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\text{=}C\text{=}CHR)]^+X^-$ remain in progress [20].

Experimental

General data

All reactions were carried out under a dry nitrogen atmosphere. IR spectra were recorded on a Mattson Polaris FT spectrometer. NMR spectra were recorded on Varian XL-300 spectrometers at ambient probe temperature and referenced as follows (ppm): ^1H, $Si(CH_3)_4$ (0.00) or residual CD_2HNO_2 (4.33); $^{13}C\{^1H\}$, $Si(CH_3)_4$ (0.0), $CDCl_3$ (77.0), or CD_3NO_2 (62.8); $^{31}P\{^1H\}$, external H_3PO_4 (0.0). When diastereomers give distinct chemical shifts, data are separated by slashes (/). Microanalyses were conducted by Atlantic Microlab.

Solvents and reagents were obtained as follows: CH_2Cl_2 and C_6H_5Cl, distilled from P_2O_5; THF and benzene, distilled from Na/benzophenone; hexane, distilled from sodium; $CDCl_3$ vacuum transferred from CaH_2; $Ph_3C^+PF_6^-$ (Aldrich), crystallized as described earlier [21]; bis(triflates) $TfO(CH_2)_nOTf$, prepared by adaptations of literature procedures [13]; ^{n}BuLi in hexane (Aldrich), standardized before use [22]; dienes (Aldrich), C_6D_6, CD_3NO_2 (Cambridge Isotopes), used as received; $HBF_4 \cdot OEt_2$ (Aldrich), standardized as described previously [23].

*$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2)_3(PPh_3)(NO)Re(\eta^5\text{-}C_5H_5)$ (**7a**)*

A Schlenk tube was charged with $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H)$ (**11**) [12] (0.116 g, 0.213 mmol), THF (5 mL), and a stir bar, and was fitted with a septum. The yellow solution was cooled to −15°C, and ^{n}BuLi in hexane (0.234 mmol) was added dropwise with stirring to give a red solution of **6**. After 0.5 h, $TfO(CH_2)_3OTf$ (0.040 g, 0.117 mmol) was added. After 5 min, the cooling bath was removed and the solution was stirred for 0.5 h. Solvent was removed under oil pump vacuum, and the residue was extracted with benzene. The extract was filtered through a small plug of Florisil that had been treated with concentrated NH_4OH (30% v/w). Solvent was removed from the filtrate by rotary evaporation, and the residue was crystallized from CH_2Cl_2/hexane. The bright yellow–orange powder was dried under oil pump vacuum to give **7a** (0.107 g, 0.164 mmol, 89%) [24*]. Anal. Found: C, 52.10; H, 4.15. $C_{49}H_{46}N_2O_2P_2Re_2$ calc.: C, 52.12; H, 4.11%. IR (KBr): $\nu(NO)$

1623s cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.62 (m, 12H of $6C_6H_5$); 7.00 (m, 18H of $6C_6H_5$); 4.74/4.70 (s, $2C_5H_5$); 2.76 (m, 2H); 2.52 (m, 2H); 2.17 (m, 2H). ^{13}C{^{1}H} NMR (C_6D_6): 137.8 (d, J(CP) = 50 Hz, *i*-Ph); 133.9 (d, J(CP) = 10 Hz, *o*-Ph); 129.4 (s, *p*-Ph) [25*]; 89.5 (s, C_5H_5); 54.9/52.4 (s, C_β); $-1.2/-1.4$ (d, J(CP) = 4/5 Hz, C_α) ppm. ^{31}P{^{1}H} NMR (C_6D_6): 28.4/27.8 (s) ppm.

$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2)_4(PPh_3)(NO)Re(\eta^5\text{-}C_5H_5)$ (**7b**)

Complex **11** (0.271 m, 0.489 mmol), ^{n}BuLi (0.538 mmol), and $TfO(CH_2)_4OTf$ (0.080 g, 0.224 mmol) were allowed to react in a procedure analogous to that given for **7a**. An identical workup gave **7b** as a bright yellow-orange powder (0.237 g, 0.207 mmol, 83%) [24*]. Anal. Found: C, 52.63; H, 4.28. $C_{50}H_{48}N_2O_2P_2Re_2$ calc.: C, 52.53; H, 4.23%. IR (KBr): ν(NO) 1624s cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.55 (m, 12H of $6C_6H_5$); 6.99 (m, 18H of $6C_6H_5$); 4.73/4.64 (s, $2C_5H_5$); 2.62 (m, 2H); 2.34 (m, 2H); 2.11 (m, 4H). ^{13}C{^{1}H} NMR (C_6D_6): 137.5 (d, J(CP) = 51 Hz, *i*-Ph); 133.8 (d, J(CP) = 10 Hz, *o*-Ph); 129.5 (s, *p*-Ph) [25*]; 89.5 (s, C_5H_5); 48.2/49.9 (s, C_β); $-7.9/-7.6$ (d, J(CP) = 5/4 Hz, C_α) ppm. ^{31}P{^{1}H} NMR (C_6D_6): 27.8/27.5 (s) ppm.

$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2)_5(PPh_3)(NO)Re(\eta^5\text{-}C_5H_5)$ (**7c**)

Complex **11** (0.119 g, 0.219 mmol), ^{n}BuLi (0.240 mmol), and $TfO(CH_2)_5OTf$ (0.040 g, 0.109 mmol) were allowed to react in a procedure analogous to that given for **7a**. An identical workup gave **7c** as a bright yellow-orange powder (0.107 g, 0.092 mmol, 84%) [24*]. IR (KBr): ν(NO) 1623s cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.57 (m, 12H of $6C_6H_5$); 7.06 (m, 18H of $6C_6H_5$); 4.67/4.64 (s, $2C_5H_5$); 2.58 (m, 2H); 2.13 (m, 6H); 1.78 (m, 2H). ^{13}C{^{1}H} NMR (C_6D_6): 137.4 (d, J(CP) = 50 Hz, *i*-Ph); 133.8 (d, J(CP) = 10 Hz, *o*-Ph); 129.6 (s, *p*-Ph) [25*]; 89.4 (s, C_5H_5); 43.1/43.7 (s, C_γ); 42.1/42.3 (s, C_β); $-8.0/-7.7$ (d, J(CP) = 5 Hz, C_α) ppm. ^{31}P{^{1}H} NMR (C_6D_6): 27.7/27.4 (s) ppm.

$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2)_8(PPh_3)(NO)Re(\eta^5\text{-}C_5H_5)$ (**7d**)

Complex **11** (0.710 g, 1.300 mmol), ^{n}BuLi (1.430 mmol), and $TfO(CH_2)_8OTf$ (0.268 g, 0.652 mmol) were allowed to react in a procedure analogous to that given for **7a**. An identical workup gave **7d** as a bright yellow-orange powder (0.624 g, 0.520 mmol, 80%) [24*]. Anal. Found: C, 54.17; H, 4.76. $C_{54}H_{56}N_2O_2P_2Re_2$ calc.: C, 54.08; H, 4.71%. IR (KBr): ν(NO) 1624s cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.55 (m, 12H of $6C_6H_5$); 7.01 (m, 18H of $6C_6H_5$); 4.623/4.618 (s, $2C_5H_5$); 2.50 (m, 2H); 2.06 (m, 6H); 1.59 (m, 8H). ^{13}C{^{1}H} NMR (C_6D_6): 137.4 (d, J(CP) = 51 Hz, *i*-Ph); 133.8 (d, J(CP) = 10 Hz, *o*-Ph); 129.6 (s, *p*-Ph) [25*]; 89.3 (s, C_5H_5); 42.6/42.5 (s, C_β); 36.6/36.7 (s, C_γ); 30.4/30.6 (s, C_δ); -8.6 (d, J(CP) = 4 Hz, C_α) ppm. ^{31}P{^{1}H} NMR (C_6D_6): 27.6 (s) ppm.

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CH(CH_2)HC=)(PPh_3)(NO)Re(\eta^5\text{-}C_5H_5)]^{2+}2PF_6^-$ (**3a**)

A Schlenk tube was charged with **7a** (0.045 g, 0.040 mmol), CH_2Cl_2 (5 mL), and a stir bar, and was fitted with a septum. The solution was cooled to -80°C, and

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* Reference with asterisk indicates a note in the list of references.

solid $Ph_3C^+PF_6^-$ (0.034 g, 0.084 mmol) was added with stirring. After 1 h, the cooling bath was removed and the solution was stirred for an additional 1 h. Solvent was removed under oil pump vacuum, and the residue was extracted with $CHCl_3$. Hexane was added, and the resulting tan powder was collected by filtration and dried under oil pump vacuum to give **3a** (0.043 g, 0.030 mmol, 76%) [24*]. Anal. Found: C, 41.75; H, 3.36. $C_{49}H_{44}F_{12}N_2O_2P_4Re_2$ calc.: C, 41.53; H, 3.13%. IR (KBr): ν(NO) 1719s; ν(PF) 841s cm^{-1}.

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CH(CH_2)_2HC=)(PPh_3)(NO)Re(\eta^5\text{-}C_5H_5)]^{2+}2PF_6^-$ *(3b)*

Complex **7b** (0.217 g, 0.190 mmol) and $Ph_3C^+PF_6^-$ (0.162 g, 0.418 mmol) were allowed to react in a procedure analogous to that given for **3a**. An identical workup gave **3b** as a tan powder (0.235 g, 0.164 mmol, 87%) [24*]. Anal. Found: C, 41.86; H, 3.28. $C_{50}H_{46}F_{12}N_2O_2P_4Re_2$ calc.: C, 41.96; H, 3.24%. IR (KBr): ν(NO) 1724s; ν(PF) 842s cm^{-1}. ^1H NMR (CD_3NO_2): δ 16.2/16.1/15.8 (ddd/ddd/m [27*], $J(HH(\beta)) = J(HH(\beta')) = 8.7$ Hz, $J(HP) = 1.6$ Hz, 2Re=CH); 7.80–7.25 (m, $6C_6H_5$); 6.17/6.13/6.07 (s/br s/s, $2C_5H_5$, *ca.* 21:45:34). $^{13}C\{^1H\}$ NMR (CD_3NO_2): 313.3 (br s, C_α); 134.6/134.2 (d, $J(CP) = 10/12$ Hz, *o*-Ph); 133.9/133.5 (s, *p*-Ph); 130.8 (m, *m*-Ph); 101.2/101.1/101.0 (s, C_5H_5) ppm. $^{31}P\{^1H\}$ NMR (CD_3NO_2): 19.0/18.4/18.1/17.9 (s, *ca.* 35:12:22:31) ppm.

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CH(CH_2)_3HC=)(PPh_3)(NO)Re(\eta^5\text{-}C_5H_5)]^{2+}2PF_6^-$ *(3c)*

Complex **7c** (0.071 g, 0.061 mmol) and $Ph_3C^+PF_6^-$ (0.048 g, 0.123 mmol) were allowed to react in a procedure analogous to that given for **3a**. An identical workup gave **3c** as a tan powder (0.070 g, 0.048 mmol, 79%) [24*]. IR (KBr): ν(NO) 1719s; ν(PF) 838s cm^{-1}. ^1H NMR (CD_3NO_2): δ 15.92/15.46 (br s, 2Re=CH); 7.65 (m, $6C_6H_5$); 6.12/6.09 (s, $2C_5H_5$); 3.20 (m, 1H); 2.62 (m, 1H); 1.28 (m, 2H); 0.88 (m, 2H). $^{13}C\{^1H\}$ NMR (CD_3NO_2): 308.9 (br s, C_α); 134.3 (*i*-Ph) [26*]; 133.9 (d, $J(CP) = 12$ Hz, *o*-Ph); 133.5 (s, *p*-Ph); 130.6 (d, $J(CP) = 8$ Hz, *m*-Ph); 100.8 (s, C_5H_5); 58.0/57.2 (s, C_β); 27.2/20.2 (s, C_γ) ppm. $^{31}P\{^1H\}$ NMR (CD_3NO_2): 18.3/19.7 (s).

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CH(CH_2)_6HC=)(PPh_3)(NO)Re(\eta^5\text{-}C_5H_5)]^{2+}2PF_6^-$ *(3d)*

Complex **7d** (0.070 g, 0.058 mmol) and $Ph_3C^+PF_6^-$ (0.048 g, 0.123 mmol) were allowed to react in a procedure analogous to that given for **3a**. An identical workup gave **3d** as a tan powder (0.081 g, 0.054 mmol, 93%) [24*]. Anal. Found: C, 43.37; H, 3.73. $C_{54}H_{54}F_{12}N_2O_2P_4Re_2$ calc.: C, 43.61; H, 3.66%. IR (KBr): ν(NO) 1718s; ν(PF) 840s cm^{-1}. ^1H NMR (CD_3NO_2): δ 16.16 (ddd [27*], $J(HH(\beta)) = J(HH(\beta')) = 8.7$ Hz, $J(HP) = 1.6$ Hz, 2Re=CH); 7.57 (m, $6C_6H_5$); 6.13 (s, $2C_5H_5$); 3.16 (m, 2H); 2.84 (m, 2H); 1.18 (m, 8H). $^{13}C\{^1H\}$ NMR (CD_3NO_2): 312.3 (br s, C_α); 134.1 (d, $J(CP) = 10$ Hz, *o*-Ph); 133.6 (s, *p*-Ph); 131.9 (*i*-Ph) [26*]; 130.7 (d, $J(CP) = 11$ Hz, *m*-Ph); 100.9 (s, C_5H_5); 59.9 (s, C_β); 29.8, 29.4 (s, C_γ, C_δ) ppm. $^{31}P\{^1H\}$ NMR (CD_3NO_2) 18.3 (s) ppm.

Representative thermolysis

A 5 mm NMR tube was charged with **3d** (0.008 g, 0.005 mmol) and C_6H_5Cl (0.5 mL). The sample was freeze–pump–thaw degassed three times. The tube was then transferred to an NMR probe that had been pre-equilibrated to 66°C. The disappearance of **3d** and the appearance of **5d**$^{2+}2PF_6^-$ were monitored by ^{31}P NMR (18.5 and 10.5 ppm). Rate constants were calculated (and probe temperatures calibrated) as described previously [7].

*$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHCH_2HC{=}CH_2)]^+BF_4^-$ (**9c**)*

A Schlenk flask was charged with $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (**12**) [28] (0.056 g, 0.100 mmol), C_6H_5Cl (5 mL), and a stir bar, and cooled to −45°C (CH_3CN/CO_2 bath). Then $HBF_4 \cdot OEt_2$ (12 μL, 0.110 mmol) was added with stirring to generate **8** [15]. After 15 min, excess 1,4-pentadiene was added. The mixture was stirred at 100°C for 36 h, and then filtered into hexane (50 mL). The resulting tan powder was collected by filtration, washed with pentane (2 × 3 mL), and dried under oil pump vacuum to give **9c** (0.066 g, 0.094 mmol, 94%; $(98 \pm 2):(2 \pm 2)$ (*RS,SR*)/(*RR,SS*)), m.p. 103–105°C dec. Anal. Found: C, 48.04; H, 4.06; N, 1.94. $C_{28}H_{28}BF_4NOPRe$ calc.: C, 48.15; H, 4.04; N, 2.01%. IR (thin film): ν(NO) 1721s cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.57 (m, 9H of $3C_6H_5$); 7.36 (m, 6H of $3C_6H_5$); 5.78 (s, C_5H_5); 5.83 (m, =CHR/free); 5.34 (dd, *J*(HH) = 1.4, 17.1 Hz, H_Z/free); 5.10 (dd, *J*(HH) = 1.4, 10.3 Hz, H_E/free); 4.47 (m, =CHR/bound); 3.11, 2.58, 2.52 (3m, CHH', CHH', CH_E/bound); 2.39 (ddd, *J*(HH) = 4.1, 11.0 Hz, *J*(HP) = 11.0 Hz, H_Z/bound). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 133.1 (d, *J*(CP) = 10 Hz, *o*-Ph); 132.2 (s, *p*-Ph); 130.3 (*i*-Ph) [26*]; 129.5 (d, *J*(CP) = 11 Hz, *m*-Ph); 137.5 (s, =CHR/free); 116.8 (s, $=CH_2$/free); 96.9 (s, C_5H_5); 49.9 (s, =CHR/bound); 42.0 (s, CH_2); 38.4 (d, *J*(CP) = 5.0 Hz, $=CH_2$/bound). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 10.2 (s) ppm.

*$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHCH_2HC{=}CH_2)(PPh_3)(NO)Re(\eta^5\text{-}C_5H_5)]^{2+}$ $2X^-$ (**5c**$^{2+}2X^-$)*

(A) A Schlenk tube was charged with **3c** (0.058 g, 0.040 mmol), C_6H_5Cl (7 mL), and a stir bar, and capped with a septum. The solution was stirred at 100°C for 24 h, and cooled to room temperature. Hexane was added, and the resulting yellowish powder was collected by filtration, and dried under oil pump vacuum to give **5c**$^{2+}2PF_6^-$ (0.052 g, 0.036 mmol, 90%) [24*]. ^1H NMR (CD_3NO_2): δ 7.57 (m, C_6H_5); 5.94/5.91/5.90/5.88 (s, C_5H_5). $^{13}C\{^1H\}$ NMR (CD_3NO_2): 134.7 (d, *J*(CP) = 10 Hz, *o*-Ph); 133.6 (s, *p*-Ph); 131.7 (d, *J*(CP) = 59 Hz, *i*-Ph); 130.8 (d, *J*(CP) = 10 Hz, *m*-Ph); 99.2/99.1/98.9/98.6 (s, C_5H_5); 52.0/50.2 (br s/s, =CHR); 47.0 (s, $-CH_2-$); 39.1/38.7/38.4/37.9 (br s, $=CH_2$) ppm. $^{31}P\{^1H\}$ NMR (CD_3NO_2): 11.9 (s) ppm.

(B) A Schlenk flask was charged with **12** (0.045 g, 0.081 mmol), C_6H_5Cl (2 mL), and a stir bar, and was cooled to −45°C. Then $HBF_4 \cdot OEt_2$ (10 μL, 0.088 mmol) was added with stirring. After 15 min, a solution of **9c** (0.056 g, 0.081 mmol) in C_6H_5Cl (3 mL) was added. The mixture was stirred at 100°C for 44 h, and then filtered into hexane (50 mL). The resulting yellow powder was collected by filtration, washed with pentane (2 × 3 mL), and dried under oil pump vacuum to give **5c**$^{2+}2BF_4^-$ (0.104 g, 0.078 mmol, 97%), m.p. 190–195°C dec. Anal. Found: C, 45.90; H, 3.75; N, 2.07. $C_{51}H_{48}B_2F_8N_2O_2P_2Re_2$ calc.: C, 46.09; H, 3.69; N, 2.11%. IR (thin film): ν(NO) 1721s cm^{-1}. ^1H NMR (CD_3NO_2): δ 7.58 (m, $6C_6H_5$); 5.94/5.91 (s, $(56 \pm 2):(44 \pm 2)$, $2C_5H_5$); 4.51 (m, 2 =CHR); 2.78, 2.64, 2.47 (3m, 2 $=CH_E$, CHH', CHH', 2 $=CH_Z$). $^{13}C\{^1H\}$ NMR (CD_3NO_2): 134.6 (d, *J*(CP) = 10

Hz, o-Ph); 133.6 (s, p-Ph); 131.6 (d, J(CP) = 59 Hz, i-Ph); 130.8 (d, J(CP) = 10 Hz, m-Ph); 99.0/98.9 (s, C_5H_5); 52.0/51.9 (s, =CHR); 47.0 (s, CH_2); 38.7/38.4 (d, J(CP) = 5.1 Hz, =CH_2) ppm. $^{31}P\{^1H\}$ NMR (CD_3NO_2) 11.9 (s) ppm.

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CH(CH_2)_4HC{=}CH_2)(PPh_3)(NO)Re(\eta^5\text{-}C_5H_5)]^{2+}2X^-$ ($\mathbf{5d}^{2+}2X^-$)

(A) A Schlenk tube was charged with **3d** (0.033 g, 0.022 mmol), C_6H_5Cl (3 mL), and a stir bar, and capped with a septum. The solution was stirred at 65°C for 17 h, and cooled to room temperature. Hexane was added, and the resulting yellowish powder was collected by filtration and dried under oil pump vacuum to give $\mathbf{5d}^{2+}2PF_6^-$ (0.032 g, 0.022 mmol, 97%) [24*]. Anal. Found: C, 43.52; H, 3.67. $C_{54}H_{54}F_{12}N_2O_2P_4Re_2$ calc.: C, 43.61; H, 3.66%. IR (KBr): ν(NO) 1717s; ν(PF) 841s cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.56 (m, 18H of $6C_6H_5$); 7.35 (m, 12H of $6C_6H_5$); 5.78/5.74 (s, $2C_5H_5$, *ca.* 67:33); 4.55 (m, 2 =CHR); 2.42, 2.01, 1.64 (3m, 4H each, 2 =CH_E, 2 =CH_Z, $(CH_2)_4$). $^{13}C\{^1H\}$ ($CDCl_3$): 133.0 (d, J(CP) = 9.9 Hz, o-Ph); 132.2 (s, p-Ph); 130.2 (d, J(CP) = 59.4 Hz, i-Ph); 129.5 (d, J(CP) = 10.7 Hz, m-Ph); 96.8 (s, C_5H_5); 51.7 (s, =CHR); 38.5, 37.6, 31.8 (s/s/d, J(CP) = 4.3 Hz, CH_2CH_2, =CH_2) ppm; minor diastereomers at 97.5, 52.1, 38.9, 37.8, 32.4 ppm. $^{31}P\{^1H\}$ NMR (C_6H_5Cl): 10.5 (s) ppm; ($CDCl_3$): 11.0/10.9 (s) ppm.

(B) Complex **12** (0.056 g, 0.100 mmol), C_6H_5Cl (2 mL), $HBF_4 \cdot OEt_2$ (12 μL, 0.110 mmol), and 1,7-octadiene (7.4 μL, 0.050 mmol) were allowed to react in a procedure analogous to that given for **9c** (15 h at 100°C). An identical workup gave $\mathbf{5d}^{2+}2BF_4^-$ (0.068 g, 0.049 mmol, 98%). IR (thin film): ν(NO) 1721vs cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.55 (m, 18H of $6C_5H_5$); 7.35 (m, 12H of $6C_6H_5$); 5.79/5.78/5.77/5.76 (s, $2C_5H_5$, *ca.* 37:35:13:15); 4.58 (m, 2 =CHR); 2.42, 2.00, 1.63 (3m, 4H each, 2 =CH_E, 2 =CH_Z, $(CH_2)_4$). $^{13}C\{^1H\}$ ($CDCl_3$): 133.1 (d, J(CP) = 9.9 Hz, o-Ph); 132.1 (s, p-Ph); 130.3 (d, J(CP) = 58.8 Hz, i-Ph); 129.5 (d, J(CP) = 10.9 Hz, m-Ph); 96.9 (s, C_5H_5); 51.8 (s, =CHR); 38.5, 37.6, 31.8 (s/s/br s, CH_2CH_2, =CH_2) ppm; minor diastereomers at 97.6, 52.3, 39.0, 37.7, 32.1 ppm. $^{31}P\{^1H\}$ ($CDCl_3$) 11.0/10.9 (s) ppm; minor diastereomer at 10.8 ppm.

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