Conversion of rhenium alkylidyne complexes that contain unsupported metal–metal double bonds into relatives that contain μ-alkylidyne ligands [1]

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Abstract

Photolysis of compounds of the type $[Re(CCMe_2R)(OR')_2]_2$ (R = Me or Ph; OR' = O^tBu, $OCMe_2(CF_3)$, or $OCMe(CF_3)_2$) in benzene with a medium pressure mercury lamp yields compounds of the type $[Re(OR')_2]_2(\mu\text{-}CCMe_2R)_2$ in an intramolecular and irreversible manner. $[Re(CCMe_2R)(OR')_2]_2$ and $[Re(OR')_2]_2(\mu\text{-}CCMe_2R)_2$ (OR' = O^tBu or $OCMe_2(CF_3)$) both react with excess carbon monoxide in several solvents to afford the dimers $[Re(OR')_2(CO)]_2(\mu\text{-}CCMe_2R)_2$ quantitatively. An X-ray study of $[Re(O^tBu)_2(CO)]_2(\mu\text{-}C^tBu)_2$ shows it to consist of two distorted trigonal bipyramids connected by two symmetrically bridging neopentylidyne ligands. The unbridged dimers of general formula $[Re(CCMe_2R)(OR')_2]_2$ do not react readily with simple substrates such as phosphines, olefins, or acetylenes, although $[Re(CCMe_2R)(O^tBu)_2]_2$ can be oxidized by iodine to yield $Re(CCMe_2R)(O^tBu)_2I_2$ in good yield. In contrast, $\{Re[OCMe(CF_3)_2]_2\}_2(\mu\text{-}C^tBu)_2$ reacts with one equivalent of phenylacetylene to give a species in which one of the two bridging alkylidyne ligands is retained.

Keywords: Rhenium; Alkylidyne complexes; Alkylidene; Alkoxide

1. Introduction

Several years ago we reported the synthesis and structures of two alkylidyne complexes with the general formula $[Re(C^tBu)(OR')_2]_2$ (OR' = O^tBu or $OCMe(CF_3)_2$) that contain an unbridged Re=Re bond [1]. (One of the structures, in which Re=Re = 2.3836(8) Å, is shown in Fig. 1 for reference.) Such compounds are unusual since there is much precedent for both alkylidynes and alkoxides to bridge metal centers; and the electron deficient nature of the metals (12e) would seem to allow one or the other to behave as a bridging ligand. In contrast, in $(Me_3SiCH_2)_3(O)Re(\mu\text{-}O)[Re(PMe_3)_4]\text{-}Re(O)_2(CH_2SiMe_3)$ [2] (in which the central metal is already six-coordinate) and complexes such as $[M(\text{oc-taethylporphyrin})]_2$ (M = Ru, Os) [3,4], there is no opportunity for ligands to bridge the metal–metal double bond, while in a compound such as $(\eta^5\text{-}C_5Me_5)(CO)_2$-

$Re=Re(CO)_2(\eta^5\text{-}C_5Me_5)$ [5,6], "semi-bridging" carbonyl ligands compensate for the 16e count on each metal. (An analysis of the bonding and energetics in "$[Re(CH)(OH)_2]_2$", "$[Re(\eta^5\text{-}C_5H_5)(CO)_2]_2$", and "$Re(CH)(OH)_2Re=Re(\eta^5\text{-}C_5H_5)(CO)_2$" has been carried out [7].) The reaction of $[Re(CCMe_2Ph)(O^tBu)_2]_2$ with two equivalents of iodine to give pentane-soluble $Re(CCMe_2Ph)(O^tBu)_2I_2$ suggested that "Re(VII)" alkylidyne complexes of the type $Re(CR)X_4$ or $Re(CR)X_2Y_2$ might be useful starting materials to prepare dimers containing unbridged Re=Re bonds, if they could be reduced to Re=Re species, and if a route to them could be found. $Re(CR)X_4$ complexes would also be of interest in their own right. Unfortunately, we have not yet been able to find a route to $Re(CR)X_4$ species, and therefore cannot anticipate exploring their chemistry or the possibility of using them as starting materials for preparing Re=Re species, even though preliminary experiments suggest that $Re(CCMe_2Ph)\text{-}(O^tBu)_2I_2$ can be reduced cleanly in THF to $[Re(CCMe_2Ph)(O^tBu)_2]_2$ by sodium amalgam. In the process of further exploring this chemistry, we have

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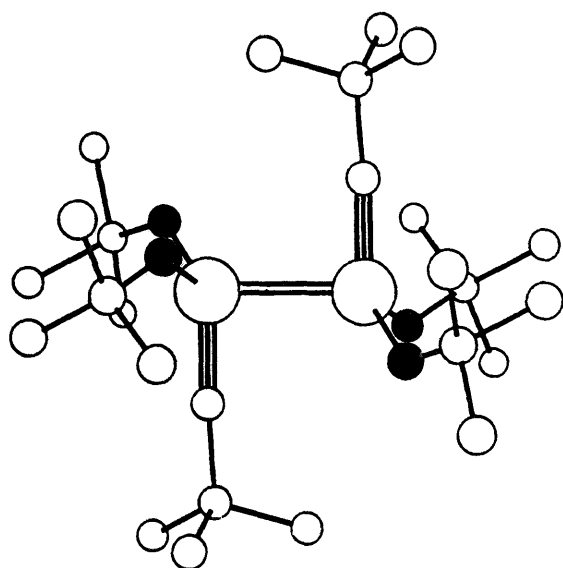[1] Dedicated to the memory of Professor H. Takaya.

Fig. 1. A Chem 3D drawing of the molecular structure of [Re(C'Bu)(O'Bu)₂]₂.

discovered a reason why a large family of Re=Re species may not be readily accessible; [Re(CCMe₂R)-(OR')₂]₂ complexes are photochemically unstable and are converted quantitatively into complexes that contain a bridging alkylidyne ligand, [Re(OR')₂]₂(μ-CCMe₂-R)₂, as shown by an X-ray crystal structure of a carbonyl adduct, [Re(O'Bu)₂(CO)]₂(μ-C'Bu)₂. These results are reported here, along with a full description of the syntheses of the Re≡Re complexes.

2. Results and discussion

When ethyl vinyl ether is added to highly concentrated solutions of Re(C'Bu)(CH'Bu)(OR')₂ (OR' = OCMe(CF₃)₂ or O'Bu) [8] in pentane or methylene chloride, or when these compounds are dissolved in

neat ethyl vinyl ether, the color immediately darkens and bright orange crystals of [Re(C'Bu)(OR')₂]₂ are deposited. Four-coordinate alkylidene complexes, syn- and anti-Re(C'Bu)[CH(OEt)][OCMe(CF₃)₂]₂, can be observed as intermediates by proton NMR, along with neohexene, the primary metathesis product. {Re(C'Bu)-[OCMe(CF₃)₂]₂}₂ forms rapidly along with primarily cis- and trans-3,3-dimethylbutenyl ethyl ether, but small amounts of cis- and trans-diethoxyethene (identified by NMR) are also formed. In contrast, the reaction of Re(C'Bu)(CH'Bu)(O'Bu)₂ with ethyl vinyl ether is slow. Over the course of two days at room temperature in pentane no intermediates were detected, [Re(C'Bu)(O'Bu)₂]₂ was isolated in 60 to 70% yield, and neohexene and cis- and trans-3,3-dimethylbutenyl ethyl ether were identified by NMR. [Re(CCMe₂Ph)-(OR')₂]₂, {Re(C'Bu)[OCMe₂(CF₃)]₂}₂, and {Re(CC-Me₂Ph)[OCMe(CF₃)₂]₂}₂ were prepared by similar methods. [Re(C'Bu)(O'Bu)₂]₂ is highly soluble in pentane whereas {Re(C'Bu)[OCMe(CF₃)₂]₂}₂ is only slightly soluble in methylene chloride. Despite the fundamental solubility difference, these two species are isostructural, as shown in X-ray diffraction studies (see Fig. 1) [1]. Carbon NMR studies also confirm that similar alkylidyne carbon atoms are present in all compounds of this type (Table 1). A rhenium–rhenium double bond is consistent with the diamagnetism of these dimers and is attractive by analogy of the Re=Re bond with the Re=C bond in alkylidene alkylidyne complexes of the type Re(CR)(CHR)(OR')₂ [8] and in terms of orbital symmetries and energetics [7].

All evidence to date suggests that the primary mechanism of forming the Re=Re compounds consists of bimolecular coupling of alkylidene ligands. For example, orange crystalline Re(C'Bu)[CH(OEt)][OCMe-(CF₃)₂]₂(THF)₂ [9] reacts with one equivalent of Re(C'Bu)(CH'Bu)[OCMe(CF₃)₂]₂ in toluene over a period of 4 h at 85°C to give {Re(C'Bu)[OCMe(CF₃)₂]₂}₂ in 90% yield and cis- and trans-3,3-dimethylbutenyl

Table 1
Chemical shifts (ppm) for compounds of the general formula [Re(CR)(OR')₂]₂, [Re(OR')₂]₂(μ-CR)₂, and Re(CCMe₂Ph)(O'Bu)₂I₂ [a]

Compound	¹H (CCMe)	¹³C (Re≡C)	¹H (OCMe)
[Re(C'Bu)(O'Bu)₂]₂ [b]	1.74	283.7	1.28
[Re(CCMe₂Ph)(O'Bu)₂]₂ [b]	2.20	282.1	1.20
{Re(C'Bu)[OCMe₂(CF₃)]₂}₂	1.65	290.8	1.29, 1.19
{Re(CCMe₂Ph)[OCMe₂(CF₃)]₂}₂	2.06	289.0	1.07, 1.00
{Re(C'Bu)[OCMe(CF₃)₂]₂}₂	1.68	298.9	1.33
[Re(O'Bu)₂]₂(μ-C'Bu)₂ [b]	2.00	333.9	1.00
[Re(O'Bu)₂]₂(μ-CCMe₂Ph) [b]	2.50	334.6	0.91
{Re[OCMe₂(CF₃)]₂}₂(μ-C'Bu)₂	1.88	342.3	1.02
{Re[OCMe₂(CF₃)]₂}₂(μ-CCMe₂Ph)₂	2.29	341.7	0.77
{Re[OCMe(CF₃)₂]₂}₂(μ-C'Bu)₂	1.88	350.6	1.04
[Re(O'Bu)₂(CO)]₂(μ-C'Bu)₂	2.01	381.7	1.53, 0.99
{Re[OCMe₂(CF₃)]₂(CO)}₂(μ-C'Bu)₂	2.06	387.6	1.65, 1.31
Re(CCMe₂Ph)(O'Bu)₂I₂	1.66	319.6	1.35

[a] All spectra were recorded in CD₂Cl₂ unless otherwise noted. [b] Recorded in C₆D₆.

ethyl ether as the major olefinic products, while Re(C^{t}Bu)[CH(OEt)][OCMe(CF$_3$)$_2$]$_2$(THF)$_2$ alone decomposes in C$_6$D$_6$ under similar conditions to give {Re(C^{t}Bu)[OCMe(CF$_3$)$_2$]$_2$}$_2$ and cis- and trans-1,2-diethoxyethylene in high yield. No olefinic products with tert-butyl groups are observed in the latter reaction, indicating that decomposition does not involve the alkylidyne unit. Since formation of a 1,3-M$_2$C$_2$ core is more consistent with M=C bond polarity, we speculate that 1,3-dimetallacycles are intermediates in these de-

composition reactions (Eq. (1)). Subsequent loss of olefin could either generate [Re(CCMe$_2$R)(OR')$_2$]$_2$ directly or monomeric Re(CCMe$_2$R)(OR')$_2$ units could be formed that quickly couple to give the dimer. In contrast, samples of Re(C^{t}Bu)(CH^{t}Bu)(OR')$_2$ (OR' = O^{t}Bu or OCMe(CF$_3$)$_2$) produce only trace amounts of trans-2,2,5,5-tetramethyl-3-hexene after being heated in solution for several hours at 120°C, a result that suggests that alkylidene coupling is most rapid when heteroatom substituents are present in relatively small alkylidenes.
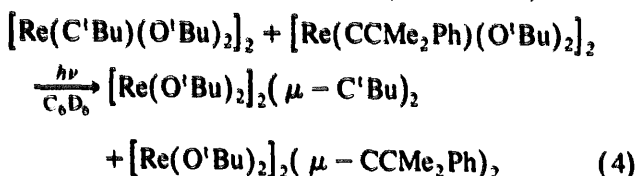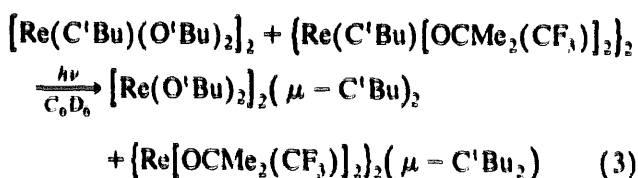
$$2Re(CCMe_2R)[CH(OEt)](OR'_2)_2(THF)_2 \xrightarrow[-4THF]{\Delta}$$

$$EtOCH=CHOEt + \{Re(CCMe_2R)[OCMe(CF_3)_2]_2\}_2 \qquad (1)$$
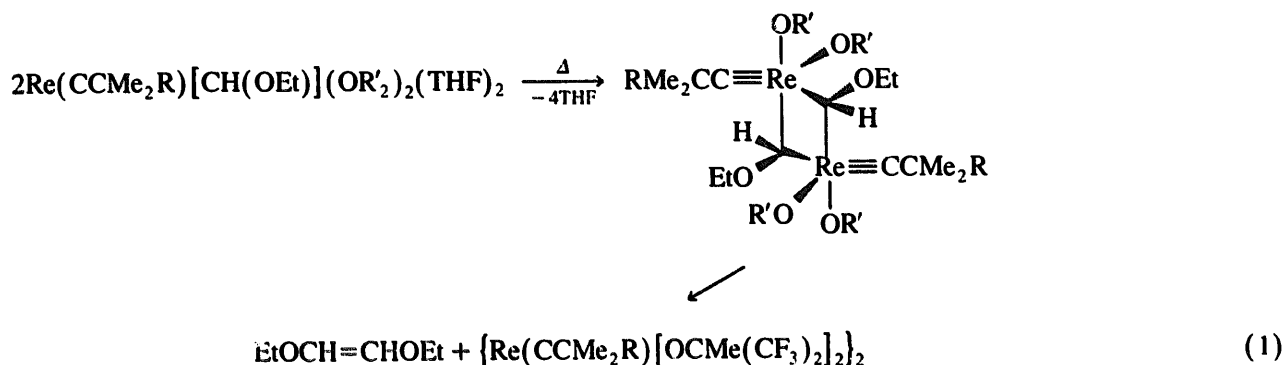
The [Re(CCMe$_2$R)(OR')$_2$]$_2$ compounds are quite robust thermally. For example, [Re(C^{t}Bu)(O^{t}Bu)$_2$]$_2$ shows little degradation after being heated for 2 days at 120°C in C$_6$D$_6$ in a sealed tube. However, upon photolysis in benzene with a medium pressure mercury lamp, dramatic changes are observed. A new compound is formed cleanly in which the alkylidyne tert-butyl resonance is found downfield by 0.2 to 0.4 ppm of that in [Re(C^{t}Bu)(O^{t}Bu)$_2$]$_2$ and the alkoxide resonances have moved upfield by 0.2 to 0.4 ppm. The inequivalent methyl groups in {Re(C^{t}Bu)[OCMe$_2$(CF$_3$)]$_2$}$_2$ become equivalent in the photolysis product. In carbon NMR spectra, the alkylidyne α-carbon atom resonance moves

downfield by around 50 ppm. These downfield ^{13}C NMR shifts are consistent with the formation of bridging alkylidyne ligands (Eq. (2)). For example, the α-carbon resonance is found between 350 and 410 ppm in W [10-13], Nb [14], and Ta [15] compounds that contain bridging alkylidyne ligands, and at 325.5 ppm in [Cp*ClRe]$_2$(μ-Cl)(μ-CC$_6$H$_5$) [16]. (NMR data for compounds reported here are listed in Table 1.) Although these alkylidyne-bridged complexes are highly crystalline, no crystals suitable for an X-ray study could be obtained. A data set was collected and solved for [Re(O^{t}Bu)$_2$]$_2$(μ-CCMe$_2$Ph)$_2$; the structure could not be refined, although the connectivity could be established as shown in Eq. (2):
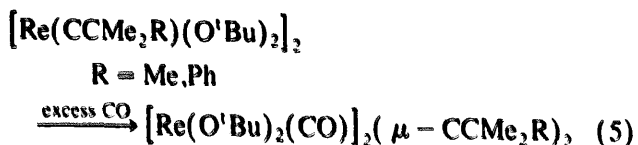

$$(2)$$
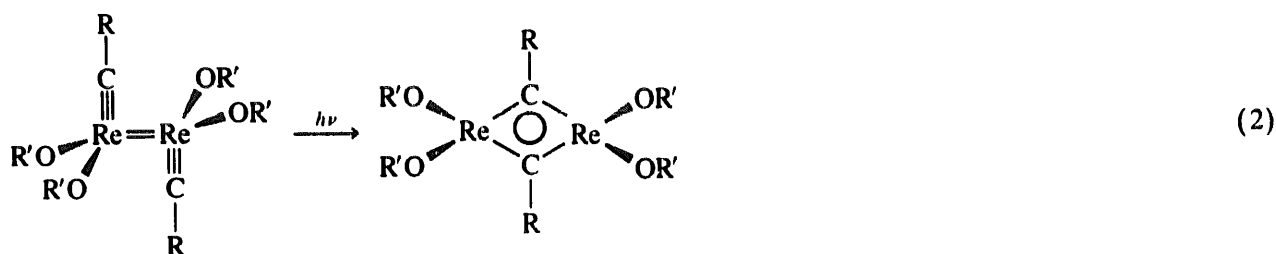
This structure is similar to that found for [Re(CH$_2$Si-Me$_3$)$_2$]$_2$(μ-CSiMe$_3$)$_2$ [17], which is a low yield ($<$ 5%) product of the reaction between ReCl$_4$(THF)$_2$ and Me$_3$SiCH$_2$MgCl. Other structurally analogous dimers in this category include [M(CH$_2$SiMe$_3$)$_2$]$_2$(μ-CSiMe$_3$)$_2$ (M = Nb, Ta) [12,14], [W(CH$_2$SiMe$_3$)$_2$]$_2$(μ-CSiMe$_3$)$_2$ [12,18], [W(OR)$_2$]$_2$(μ-CSiMe$_3$)$_2$ [10,11], and Ta(CH$_2$-SiMe$_3$)$_2$(μ-CSiMe$_3$)$_2$Ta(O-2,6-^{t}BuC$_6$H$_3$) [15].

Two experiments were performed in order to determine whether the photochemical conversion of unbridged dimers to alkylidyne-bridged dimers is intramolecular or intermolecular. An equimolar mixture of [Re(C^{t}Bu)(O^{t}Bu)$_2$]$_2$ and {Re(C^{t}Bu)[OCMe$_2$(CF$_3$)]$_2$}$_2$ was photolyzed in C$_6$D$_6$ and the appearance of the respective photodimers was monitored with time. Conversion to the alkylidyne-bridged complexes expected from an entirely *intramolecular* process proceeded at roughly comparable rates, with less than 5% of mixed alkoxides such as [Re(O^{t}Bu)$_2$](μ-C^{t}Bu)$_2${Re[OCMe$_2$ (CF$_3$)]$_2$} being observed (Eq. (3)). In a similar experiment, photolysis of an equimolar mixture of [Re(C^{t}Bu)(O^{t}Bu)$_2$]$_2$ and [Re(CCMe$_2$Ph)(O^{t}Bu)$_2$]$_2$ in C$_6$D$_6$ produced only [Re(O^{t}Bu)$_2$](μ-C^{t}Bu)$_2$ and [Re(O^{t}Bu)$_2$]$_2$(μ-CCMe$_2$Ph)$_2$ (Eq. (4)). Therefore the μ-alkylidyne complexes are formed in a process that is solely intramolecular and alkoxides do not exchange to any significant degree between any species present in these systems. We have also seen no evidence that formation of any [Re(OR')$_2$]$_2$(μ-CCMe$_2$R)$_2$ species is reversible.

$$\left[Re(C^tBu)(O^tBu)_2\right]_2 + \left\{Re(C^tBu)\left[OCMe_2(CF_3)\right]_2\right\}_2$$

$$\xrightarrow[C_6D_6]{h\nu} \left[Re(O^tBu)_2\right]_2(\mu - C^tBu)_2$$

$$+ \left\{Re\left[OCMe_2(CF_3)\right]_2\right\}_2(\mu - C^tBu_2) \qquad (3)$$

$$\left[Re(C^tBu)(O^tBu)_2\right]_2 + \left[Re(CCMe_2Ph)(O^tBu)_2\right]_2$$

$$\xrightarrow[C_6D_6]{h\nu} \left[Re(O^tBu)_2\right]_2(\mu - C^tBu)_2$$

$$+ \left[Re(O^tBu)_2\right]_2(\mu - CCMe_2Ph)_2 \qquad (4)$$

[Re(CCMe$_2$R)(O^{t}Bu)$_2$]$_2$ and [Re(O^{t}Bu)$_2$]$_2$(μ-CCMe$_2$R)$_2$ (R = Me, Ph) both react with excess carbon monoxide in several solvents to afford the dimers [Re(O^{t}Bu)$_2$(CO)]$_2$(μ-CCMe$_2$R)$_2$ (Eq. (5)) quantitatively:

$$\left[Re(CCMe_2R)(O^tBu)_2\right]_2$$

$$R = Me, Ph$$

$$\xrightarrow{excess\ CO} \left[Re(O^tBu)_2(CO)\right]_2(\mu - CCMe_2R)_2 \qquad (5)$$

The low solubility of these dimers is what allows them to be isolated, as they readily lose CO in solution. For example, when isolated [Re(O^{t}Bu)$_2$(CO)]$_2$(μ-CCMe$_2$-R)$_2$ is redissolved in C$_6$D$_6$, a mixture containing ap-

proximately 20% of [Re(O^{t}Bu)$_2$]$_2$(μ-CCMe$_2$-R)$_2$, 20% [Re(O^{t}Bu)$_2$(CO)]$_2$(μ-CCMe$_2$R)$_2$, and 60% of a third species was observed. An infrared spectrum of this mixture showed a strong terminal carbonyl stretch at 1992 cm^{-1} (1990 cm^{-1} when R = Me) which is assigned to the carbonyl ligands of [Re(O^{t}Bu)$_2$(CO)]$_2$(μ-CCMe$_2$R)$_2$ and a second carbonyl stretch at 1962 cm^{-1} (1959 cm^{-1} when R = Me) which is assigned to the third species. Only [Re(O^{t}Bu)$_2$(CO)]$_2$(μ-CCMe$_2$R)$_2$ is observed in the IR and NMR spectra in the presence of excess CO. This suggests that the remaining species is a monocarbonyl adduct, perhaps [Re(O^{t}Bu)$_2$(CO)](μ-CCMe$_2$R)$_2$[Re(O^{t}Bu)$_2$]. (Monoadducts of complexes such as W$_2$(CH$_2$SiMe$_3$)$_4$(μ-CSiMe$_3$)$_2$ are known [10].) Only one kind of alkoxide resonance is observed in NMR spectra of the proposed monocarbonyl species, indicating that the CO ligand may be rapidly exchanging with free CO or between the two metal centers of the dimer. Low temperature NMR studies were not feasible due to the low solubilities of these species.

The ^{13}C NMR spectrum of [Re(O^{t}Bu)$_2$(CO)]$_2$(μ-C^{t}Bu)$_2$, obtained in the presence of excess CO, shows an alkylidyne resonance at 381.7 ppm and a carbonyl resonance at 186.1 ppm. Exchange of coordinated CO with free CO does not take place rapidly on the ^{13}C NMR time scale. A ^{13}C NMR spectrum of [Re(O^{t}Bu)$_2$(CO)]$_2$(μ-CCMe$_2$Ph)$_2$ could not be obtained due to the low solubility of this compound in CD$_2$Cl$_2$ and other non-coordinating solvents.

X-ray quality crystals of [Re(O^{t}Bu)$_2$(CO)]$_2$(μ-C^{t}Bu)$_2$ were obtained by adding excess CO to a CD$_2$Cl$_2$ solution of [Re(C^{t}Bu)(O^{t}Bu)$_2$]$_2$. The structure consists of two distorted trigonal bipyramids connected by two symmetrically bridging neopentylidyne ligands, as shown in Figs. 2 and 3. Most of the distortion involves the axial alkoxide tipping away from the adjacent metal center by approximately 15° (see Fig. 3). The planar Re–C(1)–Re*–C(1)* unit is almost square, and the alkylidyne *tert*-butyl groups lie in the Re$_2$C$_2$ plane. The
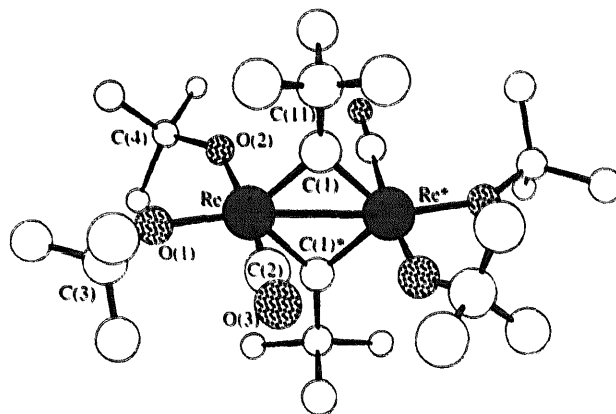
Fig. 2. An ORTEP drawing of the structure of [Re(O^{t}Bu)$_2$(CO)]$_2$(μ-C^{t}Bu)$_2$.
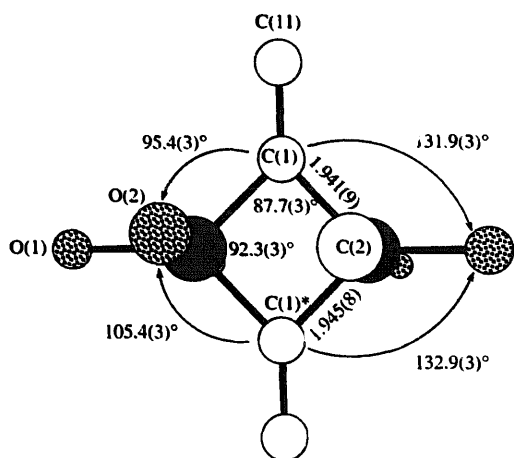
Fig. 3. A partial Chem 3D drawing of the structure of [Re(O^{t}Bu)$_2$(CO)]$_2$(μ-C^{t}Bu)$_2$ showing selected bond lengths and angles.

Re–Re distance of 2.6921(7) Å should be compared with the metal–metal distance in other compounds of this general type, examples being (WCp*Me)$_2$(μ-CMe)$_2$ (2.606(1) Å) [13], W$_2$(O^{i}Pr)$_4$(μ-CSiMe$_3$)$_2$ (2.622(2) Å) [10], Re$_2$(μ-CSiMe$_3$)$_2$(CH$_2$SiMe$_3$)$_4$ (2.557(1) Å) [17], and W$_2$(μ-CSiMe$_3$)$_2$(CH$_2$SiMe$_3$)$_4$ (2.521(2) and 2.549(2) Å) [18]. Other bond lengths and angles are not much different from those in the parent species [Re(C^{t}Bu)(O^{t}Bu)$_2$]$_2$ [1] (Table 2).

Reaction of {Re(C^{t}Bu)[OCMe$_2$(CF$_3$)]$_2$}$_2$ with excess carbon monoxide yields {Re[OCMe$_2$(CF$_3$)]$_2$(CO)}$_2$(μ-C^{t}Bu)$_2$, which can be isolated analytically pure in high yield as orange crystals. Unlike the [Re(O^{t}Bu)$_2$(CO)]$_2$-(μ-CCMe$_2$R)$_2$ species, {Re[OCMe$_3$(CF$_3$)]$_2$(CO)}$_2$(μ-CCMe$_3$)$_2$ does not lose CO in vacuo, and a satisfactory elemental analysis was obtained. The ^{13}C NMR spec-
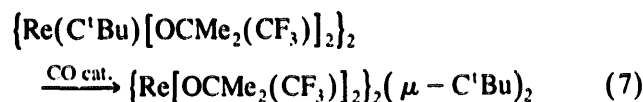
Table 2
Selected intramolecular distances (Å) and angles (°) for the non-hydrogen atoms in [Re(O^{t}Bu)$_2$(CO)]$_2$(μ-C^{t}Bu)$_2$

Distances			
Re–Re	2.6921(7)	Re–C(2)	1.99(1)
Re–O(1)	1.921(6)	O(1)–C(3)	1.42(1)
Re–O(2)	1.934(6)	O(2)–C(4)	1.420(9)
Re–C(1)	1.945(8)	O(3)–C(2)	1.13(1)
Re–C(1)*	1.941(9)	C(1)–C(11)	1.49(1)

Angles			
Re*–Re–O(1)	166.9(2)	O(2)–Re–C(2)	171.1(3)
Re*–Re–O(2)	105.1(2)	C(1)–Re–C(1)*	92.3(3)
Re*–Re–C(1)	46.1(3)	C(1)–Re–C(2)	83.4(4)
Re–Re*–C(1)*	46.2(2)	C(1)*–Re–C(2)	85.5(4)
Re*–Re–C(2)	82.0(3)	Re–O(1)–C(3)	145.8(6)
O(1)–Re–O(2)	88.0(3)	Re–O(2)–C(4)	144.1(7)
O(1)–Re–C(1)	131.9(3)	Re–C(1)–Re*	87.7(3)
O(1)–Re–C(1)*	132.9(3)	Re–C(1)–C(11)	138.2(7)
O(1)–Re–C(2)	84.9(3)	Re–C(1)*–C(11)*	134.1(7)
O(2)–Re–C(1)	105.4(3)	Re–C(2)–O(3)	179.6(9)
O(2)–Re–C(1)*	95.4(3)		

trum features the bridging alkylidyne α-carbon resonance at 387.6 ppm, 45 ppm downfield of the parent bridging alkylidyne (Table 1). Spectral data are all consistent with a structure analogous to that determined for [Re(O^{t}Bu)$_2$(CO)]$_2$(μ-C^{t}Bu)$_2$. A strong terminal carbonyl stretch is observed at 2027 cm^{-1} (CH$_2$Cl$_2$) in the infrared spectrum. When this species is isolated and redissolved in C$_6$D$_6$, there is no evidence of ready CO loss or fluxional behavior at 25°C, but in CD$_2$Cl$_2$ a second species is formed rapidly that appears to be a monocarbonyl adduct (ν_{CO} = 1991 cm^{-1} in CH$_2$Cl$_2$), analogous to that proposed in the O^{t}Bu system above. In order to test this hypothesis, an equimolar mixture of {Re(C^{t}Bu)[OCMe$_2$(CF$_3$)]$_2$}$_2$ and {Re[OCMe$_2$(CF$_3$)]$_2$-(CO)}2(μ-C^{t}Bu)$_2$ was dissolved in CD$_2$Cl$_2$. After 12 h a 1:2:1 mixture of {Re[OCMe$_2$(CF$_3$)]$_2$}$_2$(μ-C^{t}Bu)$_2$, {Re[OCMe$_2$(CF$_3$)]$_2$}$_2$(μ-C^{t}Bu)$_2$(CO) and {Re[OcMe$_2$-(CF$_3$)]$_2$(CO)}$_2$(μ-C^{t}Bu)$_2$ had formed, consistent with slow CO exchange (Eq. (6)). Likewise, when one equivalent of carbon monoxide was added to {Re(C^{t}Bu)[OCMe$_2$(CF$_3$)]$_2$}$_2$ in CD$_2$Cl$_2$, a similar mixture was obtained. We cannot discount the possibility that dichloromethane is behaving as a ligand [19–22] and thereby stabilizing the monocarbonyl species.

$$\{Re(C^tBu)[OCMe_2(CF_3)]_2\}_2$$

$$+\{Re[OCMe_2(CF_3)]_2(CO)\}_2(\mu - C^tBu)_2$$

$$\rightleftharpoons 2\{Re[OCMe_2(CF_3)]_2\}_2(\mu - C^tBu)_2(CO) \quad (6)$$
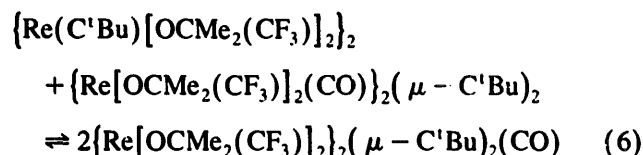
In the case of [Re(O^{t}Bu)$_2$(CO)]$_2$(μ-C^{t}Bu)$_2$, reversible binding of CO serves to catalyze the conversion of [Re(C^{t}Bu)(O^{t}Bu)$_2$]$_2$ to [Re(O^{t}Bu)$_2$]$_2$(μ-C^{t}Bu)$_2$. In the case of {Re(C^{t}Bu)[OCMe$_2$(CF$_3$)]$_2$}$_2$, CO binds much more tightly, but an analogous, slower conversion can be observed. Addition of 0.10 equiv. of CO to a C$_6$D$_6$ solution of {Re(C^{t}Bu)[OCMe$_2$(CF$_3$)]$_2$}$_2$ resulted in the immediate formation of 0.10 equiv. of {Re[OCMe$_2$-(CF$_3$)]$_2$}$_2$(μ-C^{t}Bu)$_2$(CO). The reaction was kept in the dark and monitored over several days; the amount of {Re[OCMe$_2$(CF$_3$)]$_2$}$_2$(μ-C^{t}Bu)$_2$(CO) remained relatively constant, while {Re[OCMe$_2$(CF$_3$)]$_2$}$_2$(μ-4-C^{t}Bu)$_2$ formed at the expense of {Re(C^{t}Bu)[OCMe$_2$(CF$_3$)]$_2$}$_2$ (Eq. 7):

$$\{Re(C^tBu)[OCMe_2(CF_3)]_2\}_2$$

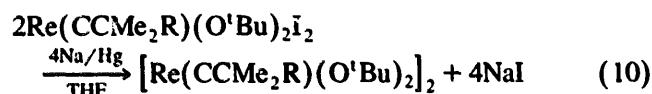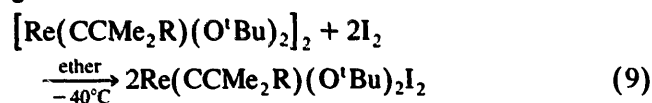$$\xrightarrow{\text{CO cat.}} \{Re[OCMe_2(CF_3)]_2\}_2(\mu - C^tBu)_2 \quad (7)$$

The unbridged dimers of general formula [Re(CCMe$_2$R)(OR')$_2$]$_2$ are surprisingly robust. Other than an inherent tendency to be converted into alkylidyne-bridged dimers upon photolysis, they do not exhibit a broad range of reactivity. Simple donor ligands such as tetrahydrofuran, pyridine, or trimethylphosphine do not react with [Re(CCMe$_2$R)(OR')$_2$]$_2$ species readily at 25°C in C$_6$D$_6$, even upon photolysis of the reaction

mixtures, in which case $[Re(OR')_2]_2(\mu\text{-}CCMe_2R)_2$ is the only observed product. $\{Re(C^tBu)[OCMe_2(CF_3)]_2\}_2$ does not react with several equivalents of pyridine in C_6D_6, but dissolution in neat pyridine leads to decomposition and an intense purple solution from which no stable species could be isolated. No reaction is observed between $[Re(C^tBu)(OR')_2]_2$ complexes and ethylene, norbornene, dicyanoethylene, pentafluorostyrene, neohexene, or ethyl vinyl ether, and upon photolysis of such reaction mixtures only conversion of the Re≡Re complex to the corresponding alkylidyne-bridged species was observed. Azobenzene, benzaldehyde, 1,3-butadiene, and $^tBuHC=N\text{-}2,6\text{-}Me_2C_6H_3$ also failed to react readily with $\{Re(C^tBu)[OCMe(CF_3)_2]_2\}_2$, as did 2-butyne, phenylacetylene, 3-hexyne, or bis(trimethylsilyl)acetylene, all in C_6D_6 in the dark.

In contrast, $\{Re[OCMe(CF_3)_2]_2\}_2(\mu\text{-}C^tBu)_2$ does react with phenylacetylene or 2-butyne to give a mixture of two products. The quantitative reaction between $\{Re[OCMe(CF_3)_2]_2\}_2(\mu\text{-}C^tBu)_2$ and phenylacetylene produced the products in an 87:13 ratio. The major isomer could be selectively crystallized from this mixture. Elemental analysis and NMR data suggest that only one equivalent of phenylacetylene has been incorporated per two rheniums, and that according to NMR the empirical formula is "$Re_2[OCMe(CF_3)_2]_2[OCMe(CF_3)_2]_2(C^tBu)(PhC=CH)$". The "acetylene" proton is observed as a singlet at δ 11.37 (C_6D_6) in the proton NMR spectrum. The ^{13}C NMR spectrum features a resonance for only one bridging alkylidyne carbon at 350.5 ppm and resonances at 137.2, 199.1, and 160.8 ppm ($J_{CH} = 178$ Hz) for the remaining "alkylidyne" and two "acetylene" carbon atoms. Therefore phenylacetylene appears to have reacted with only one of the two alkylidyne ligands in $\{Re[OCMe(CF_3)_2]_2\}_2(\mu\text{-}C^tBu)_2$. In the absence of an X-ray study, we can only speculate as to the nature of this species. There is precedent for the "1,3-dimetallaallyl" structure shown in Eq. (8) in tungsten chemistry involving $W_2(\mu\text{-}CSiMe_3)_2$ species [10], and the ^{13}C NMR chemical shifts of the backbone of the 1,3-dimetallaallyl fragment in such species are similar to those observed here.
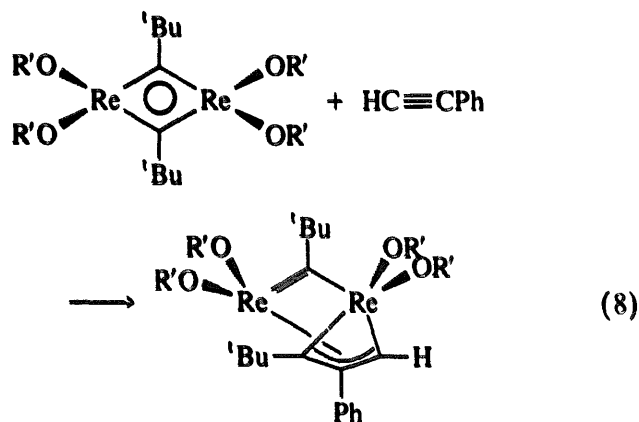
The metal–metal bonded complexes that contain tert-butoxide ligands can be oxidized. Addition of iodine to a $-40°C$ ethereal solution of $[Re(CCMe_2R)(O^tBu)_2]_2$ (R = Me, Ph) produces $Re(CCMe_2R)(O^tBu)_2I_2$ in good yield (Eq. (9)). Surprisingly, addition of iodine to solutions of $\{Re(C^tBu)[OCMe_2(CF_3)]_2\}_2$ or $\{Re(C^tBu)[OCMe(CF_3)_2]_2\}_2$ did not result in any appreciable reaction, consistent with the presence of more electron withdrawing ligands and consequently a greater resistance to oxidation. Preliminary studies suggest that reduction of $Re(CCMe_2R)(O^tBu)_2I_2$ with 2.1 equiv. of sodium amalgam in THF results in the reformation of the parent complex in high yield (Eq. (10)). Therefore if a route to $Re(CCMe_2R)(OR')_2X_2$ species could be found, reduction to Re≡Re species could be a relatively general reaction.

$$[Re(CCMe_2R)(O^tBu)_2]_2 + 2I_2$$

$$\xrightarrow[-40°C]{ether} 2Re(CCMe_2R)(O^tBu)_2I_2 \qquad (9)$$

$$2Re(CCMe_2R)(O^tBu)_2I_2$$

$$\xrightarrow[THF]{4Na/Hg} [Re(CCMe_2R)(O^tBu)_2]_2 + 4NaI \qquad (10)$$

3. Conclusions

Complexes of the type $[Re(CCMe_2R)(OR')_2]_2$ do not react readily with a variety of simple reagents, but are susceptible to formation of complexes that contain bridging alkylidyne ligands, $[Re(OR')_2]_2(\mu\text{-}CCMe_2R)_2$, either in an irreversible, intramolecular, photochemical reaction, or in a ligand-catalyzed thermal reaction. So far, exploration of such phenomena, and what appears to be a greater reactivity of $[Re(OR')_2]_2(\mu\text{-}CCMe_2R)_2$ species relative to $[Re(CCMe_2R)(OR')_2]_2$ species, has been limited by the long and indirect synthesis of $[Re(CCMe_2R)(OR')_2]_2$. Preliminary experiments suggest that if a route to Re(VII) monoalkylidyne complexes, e.g. $Re(CCMe_2R)(OR')_2(halide)_2$, can be designed, then their two electron reduction could be a relatively direct route to Re≡Re species.

4. Experimental details

All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or using standard Schlenk techniques unless otherwise specified. Pentane was washed with sulfuric/nitric acid (95/5 v/v), sodium bicarbonate and then water, stored over calcium chloride, and then distilled from sodium benzophenone ketyl under nitrogen. Reagent grade diethyl ether, tetrahydrofuran, toluene, benzene and 1,2-dimethoxyethane were distilled from sodium benzophenone ketyl under nitrogen. Reagent grade methylene chloride was distilled from calcium hydride under nitro-

$$\qquad (8)$$

gen. Tetrahydrofuran-d_8 was freshly vacuum distilled from sodium benzophenone ketyl. All other NMR solvents were deoxygenated by sparging with nitrogen and then stored over activated molecular sieves (Linde, 3 Å) in the drybox.

Ethyl vinyl ether (Aldrich) was degassed, vacuum transferred, passed through a column of activated alumina and then stored at −40°C in the drybox. Carbon monoxide (Mattheson, 99.5%) was used as received. Phenylacetylene (Aldrich) was passed through a column of activated alumina and stored at −40°C in the drybox. 2-Butyne (Farchan) was vacuum transferred and stored at −40°C in the drybox.

Re(CCMe$_2$R)(CHCMe$_2$R)(OR')$_2$ compounds (R = Me, Ph; OR' = O^{t}Bu, OCMe$_2$(CF$_3$), OCMe(CF$_3$)$_2$) were prepared by published methods [8].

4.1. [Re(C^{t}Bu)(O^{t}Bu)$_2$]$_2$

Ethyl vinyl ether (0.23 ml, 2.4 mmol) was added to a solution of Re(C^{t}Bu)(CH^{t}Bu)(O^{t}Bu)$_2$ (0.57 g, 1.2 mmol) in 2 ml of CH$_2$Cl$_2$. The dark red solution was left in a capped vial away from light for two days and then reduced to dryness in vacuo. Cooling a saturated pentane solution afforded large dark red crystals (0.27 g, 58%). ^{1}H NMR (C$_6$D$_6$): δ 1.74 (s, 18, CCMe$_3$), 1.28 (s, 36, OCMe$_3$). ^{13}C NMR (C$_6$D$_6$): δ 283.7 (CCMe$_3$), 77.0 (OCMe$_3$), 53.2 (CMe$_3$), 33.8 (OCMe$_3$), 29.4 (CCMe$_3$). Anal. Found: C, 38.94; H, 6.84. ReC$_{13}$H$_{17}$O$_2$ Calc.: C, 38.88; H, 6.78%.

4.2. [Re(CCMe$_2$Ph)(O^{t}Bu)$_2$]$_2$

Excess ethyl vinyl ether (0.35 ml, 3.7 mmol) was added to 1.1 g (1.8 mmol) Re(CCMe$_2$Ph)(CHCMe$_2$Ph)(O^{t}Bu)$_2$ in 2 ml of pentane. The reaction mixture was kept at room temperature for two days and the solvent was removed in vacuo to afford a dark red solid. This solid was recrystallized from cold pentane to afford dark red cubes (0.53 g, 63%). ^{1}H NMR (C$_6$D$_6$): δ 8.01 (d, 4, CMe$_3$), 7.31 (t, 4, C$_m$), 7.13 (t, 2, C$_p$), 2.20 (s, 12, CMe$_2$Ph), 1.20 (s, 36, OCMe$_3$). ^{13}C NMR (C$_6$D$_6$): δ 282.1 (CCMe$_3$), 147.3 (C$_i$), 128.4 and 127.4 (C$_{o,m}$), 126.6 (C$_p$), 78.0 (OCMe$_3$), 60.3 (CMe$_2$Ph), 33.9 (OCMe$_3$), 29.9 (CMe$_2$Ph). Anal. Found: C, 46.76; H, 6.38. ReC$_{18}$H$_{29}$O$_2$ Calc.: C, 46.63; H, 6.30%.

4.3. {Re(C^{t}Bu)[OCMe$_2$(CF$_3$)]$_2$}$_2$

Ethyl vinyl ether (0.36 ml, 3.75 mmol) was added to a room temperature solution of Re(C^{t}Bu)(CH^{t}Bu)[OCMe$_2$(CF$_3$)]$_2$ (1.45 g, 2.5 mmol) in 1 ml of pentane. Orange crystals of the product immediately fell out of solution. After 20 min the crystals were collected and washed with pentane to afford bright orange crystals (0.92 g, 72%). ^{1}H NMR (CD$_2$Cl$_2$): δ 1.65 (s, 18,

CMe$_3$), 1.29 and 1.19 (s, 12 each, CMe$_2$CF$_3$). ^{13}C NMR (CD$_2$Cl$_2$): δ 290.8 (CCMe$_3$), 126.9 (CF$_3$, J_{CF} = 284 Hz), 79.2 (OCMe$_2$CF$_3$), 54.9 (CMe$_3$), 29.2 (CMe$_3$), 27.6 and 25.7 (CMe$_2$CF$_3$). ^{19}F NMR (C$_6$D$_6$): δ 24.10. Anal. Found: C, 30.87; H, 3.86. ReC$_{13}$H$_{21}$F$_6$O$_2$ Calc.: C, 30.65; H, 4.15%.

4.4. {Re(CCMe$_2$Ph)[OCMe$_2$(CF$_3$)]$_2$}$_2$

Neat ethyl vinyl ether (0.8 ml) was added to solid Re(CCMe$_2$Ph)(CHCMe$_2$Ph)[OCMe$_2$(CF$_3$)]$_2$ (0.63 g, 0.89 mmol) at room temperature. Orange crystals of the product fell out of the solution within 5 min, and the solvents were then removed in vacuo. The crystals were washed with 4 × 2 ml of pentane to afford 0.37 g (71%) of analytically pure material. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.68 (d, 4, H$_o$), 7.21 (t, 4, H$_m$), 7.06 (t, 2, H$_p$), 2.06 (s, 12, CMe$_2$Ph), 1.07 and 1.00 (s, 12 each, CMe$_2$CF$_3$). ^{13}C NMR (CD$_2$Cl$_2$): δ 289.0 (CCMe$_2$Ph), 145.6 (C$_i$), 128.9 and 127.1 (C$_{o,m}$), 127.3 (C$_p$), 127.0 (CF$_3$, J_{CF} = 286 Hz), 79.8 (OCMe$_2$CF$_3$), 61.7 (CMe$_2$Ph), 29.1 (CMe$_2$Ph), 27.2 and 25.5 (CMe$_2$CF$_3$). ^{19}F NMR (C$_6$D$_6$): δ 24.10. Anal. Found: C, 38.16; H, 4.25. ReC$_{18}$H$_{23}$F$_6$O$_2$ Calc.: C, 37.82; H, 4.06%.

4.5. {Re(C^{t}Bu)[OCMe(CF$_3$)$_2$]$_2$}$_2$

Excess ethyl vinyl ether (0.53 ml, 5.5 mmol) was added to 1.26 g (1.83 mmol) Re(C^{t}Bu)(CH^{t}Bu)[OCMe$_2$(CF$_3$)]$_2$ in 2 ml of pentane. After 30 min of standing at room temperature, orange crystals of the product began to fall out of the dark red solution. After 12 h these were collected and washed with pentane to afford bright orange prisms (0.49 g, 44%, two crops). ^{1}H NMR (CD$_2$Cl$_2$): δ 1.68 (s, 18, CMe$_3$), 1.33 (s, 12, CMe(CF$_3$)$_2$). ^{13}C NMR (CD$_2$Cl$_2$): δ 298.9 (CCMe$_3$), 123.7 and 123.0 (CF$_3$, J_{CF} = 287, 288 Hz), 52.7 (CMe$_3$), 29.1 (CMe$_3$), 20.7 (CMe(CF$_3$)$_2$), the resonance for OCMe(CF$_3$)$_2$ was not located. ^{19}F NMR (CD$_2$Cl$_2$): δ 28.39. Anal. Found: C, 25.13; H, 2.62. ReC$_{13}$H$_{15}$F$_{12}$O$_2$ Calc.: C, 25.29; H, 2.45%.

4.6. [Re(O^{t}Bu)$_2$]$_2$(μ-C^{t}Bu)$_2$

This compound was prepared in quantitative yield by photolysis of [Re(C^{t}Bu)(O^{t}Bu)$_2$]$_2$ in benzene with a medium pressure mercury lamp. ^{1}H NMR (C$_6$D$_6$): δ 2.0 (s, 18, CCMe$_3$), 1.00 (s, 36, OCMe$_3$). ^{13}C NMR (C$_6$D$_6$): δ 333.9 (CCMe$_3$), 79.1 (OCMe$_3$), 49.7 (CMe$_3$), 33.0 (OCMe$_3$), 31.8 (CCMe$_3$).

4.7. [Re(O^{t}Bu)$_2$]$_2$(μ-CCMe$_2$Ph)$_2$

This compound was prepared in quantitative yield from [Re(CCMe$_2$Ph)(O^{t}Bu)$_2$]$_2$ by photolysis in benzene with a medium pressure mercury lamp. ^{1}H NMR

C, 30.95; H, 2.82. ReC$_{17}$H$_{18}$F$_{12}$O$_2$ Calc.: C, 30.54; H, 2.71%.

This compound can also be synthesized by addition of excess CO to a solution of {Re[OCMe$_2$(CF$_3$)]$_2$}$_2$(μ-C^{t}Bu)$_2$.

4.14. Observation of {Re[OCMe$_2$(CF$_3$)]$_2$}$_2$(μ-C^{t}Bu)$_2$(CO)

A solution of {Re[OCMe$_2$(CF3)]$_2$}$_2$(μ-C^{t}Bu)$_2$ (25 mg, 0.022 mmol) in 600 μl of CD$_2$Cl$_2$ was placed in a septum-capped NMR tube, and one equivalent of CO (g) (0.48 ml, 0.022 mmol) was added via syringe. The solution was shaken periodically during a period of 5 h, after which time the proton NMR showed a mixture of {Re[OCMe$_2$(CF$_3$)]$_2$(CO)}$_2$(μ-C^{t}Bu)$_2$ (vide supra), {Re[OCMe$_2$(CF$_3$)]$_2$}$_2$(μ-C^{t}Bu)$_2$(CO), and {Re[OCMe$_2$-(CF$_3$)]$_2$}$_2$(μ-C^{t}Bu)$_2$ in a 23:42:35 ratio. ^{1}H NMR (CD$_2$Cl$_2$): δ 2.00 (s, 18, CMe$_3$), 1.43 and 1.19 (br s, 12 each, OCMe$_2$(CF$_3$)). ^{13}C NMR (CD$_2$Cl$_2$): δ 362.8 (C^{t}Bu), 191.1 (CO), 126.5 (CF$_3$, J_{CF} = 287 Hz), 81.9 (OCMe$_2$(CF$_3$)), 54.9 (CMe$_3$), 31.3 (CMe$_3$), 24.8 (OCMe$_2$(CF$_3$)). ^{19}F NMR (CD$_2$Cl$_2$): δ 23.17 (br s). IR (CH$_2$Cl$_2$, cm^{-1}) 1991 (m, CO).

4.15. Reaction of {Re[OCMe(CF$_3$)$_2$]$_2$}$_2$(C^{t}Bu)$_2$ with PhC≡CH

To a solution of {Re(C^{t}Bu)[OCMe(CF$_3$)$_2$]$_2$}$_2$ (190 mg, 0.16 mmol) in 10 ml of benzene was added excess phenylacetylene (34 μl, 0.31 mmol). The solution was placed in a Pyrex bomb with Teflon stopcock and photolyzed (medium pressure Hg lamp) for 3 h. The reaction was then allowed to stir overnight and the solvent was then removed in vacuo to afford red microcrystalline product in quantitative yield. The proton NMR showed two isomers of product, the major one comprising 87% of the mixture. The major one was selectively crystallized from cold methylene chloride. Major isomer. ^{1}H NMR (CD$_2$Cl$_2$): δ 11.58 (s, 1, HCCPh), 7.79 (d, 2, H$_{ortho}$), 7.63 (t, 2, H$_{meta}$), 7.18 (t, 1, H$_{para}$), 2.20 and 0.91, (s, 6 each, OCMe(CF$_3$)$_2$), 1.89 and 0.84 (s, 9, each, CMe$_3$). ^{13}C NMR (CD$_2$Cl$_2$): δ 350.5 (CCMe$_3$ (bridging)), 199.1 (PhCCH), 168.7 (C$_{ipso}$), 160.8 (d, PhCCH, J_{CH} = 178 Hz), 131.7 and 129.4 (C$_{ortho,meta}$), 137.2 (CCMe$_3$ (ring)), 130.3 (C$_{para}$), 125 (several overlapping CF$_3$ resonances), 90.8 and 87.2 (OCMe(CF$_3$)$_2$), 56.7 and 46.7 (CMe$_3$), 33.5 and 29.8 (CMe$_3$), 20.0 and 18.2 (OCMe(CF$_3$)$_2$). No IR bands associated with either C=C or C≡C bonds were observed. Anal. Found: C, 30.95; H, 2.82. ReC$_{17}$H$_{18}$F$_{12}$O$_2$ Calc.: C, 30.54; H, 2.71%.

The minor isomer was only observed by proton NMR. Partial ^{1}H NMR (CD$_2$Cl$_2$): δ 11.22 (s, 1, HC-CPh), 1.64 and 1.36 (s, 9 each, CMe$_3$), 1.60 and 1.10, (s, 6 each, OCMe(CF$_3$)$_2$).

4.16. Re(CCMe$_2$Ph)(O^{t}Bu)$_2$I$_2$

A cold solution of iodine (96 mg, 0.39 mmol) in 2 ml of diethyl ether was added to a −40°C solution of [Re(CCMe$_2$Ph)(O^{t}Bu)$_2$]$_2$ (0.18 g, 0.19 mmol) in 3 ml of diethyl ether. The reaction was stirred at room temperature for 45 min and then the solvent was removed in vacuo. The red solid was extracted with pentane and the solution was filtered and the filtrate cooled to afford analytically pure vermillion crystals which were collected and washed with 3 ml of cold pentane; yield 0.18 g (66%). ^{1}H NMR (C$_6$D$_6$): δ 7.53 (d, 2, H$_o$), 7.17 (t, 2, H$_m$), 7.02 (t, 1, H$_p$), 1.66 (s, 6, CCMe$_2$Ph), 1.35 (s, 18, OCMe$_3$). ^{13}C NMR (C$_6$D$_6$): δ 319.6 (CCMe$_2$Ph), 145.6 (C$_i$), 128.9 and 127.2 (C$_{o,m}$), 93.9 (OCMe$_3$), 58.7 (CCMe$_3$), 30.0 (CMe$_2$Ph), 29.5 (OCMe$_3$). Anal. Found: C, 30.13; H, 4.04. ReC$_{18}$H$_{29}$O$_2$I$_2$ Calc.: C, 30.13; H, 4.07%.

4.17. X-ray study of [Re(O^{t}Bu)$_2$(CO)]$_2$(μ-C^{t}Bu)$_2$

An orange prismatic crystal was mounted on a glass fiber. All measurements were made on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range 25° < 2θ < 32°, corresponded to a monoclinic cell. Based on the systematic absences of h0l: l ≠ 2n and 0k0: k ≠ 2n, and the successful solution and refinement of the structure, the space group was determined to be P2$_1$/c; a = 10.634(2) Å, b = 9.788(1) Å, c = 16.508(2) Å, β = 102.85°, V = 1675.2(8) Å^3, Z = 4, FW = 429.57, and ρ = 1.703 g cm^{-3}. The data were collected using the ω–2θ scan technique to a maximum 2θ value of 54.9°. A total of 4274 reflections was collected. No crystal decay was observed. An empirical absorption correction using DIFABS [23] was applied which resulted in transmission factors ranging from 0.84 to 1.35. The data were corrected for Lorentz and polarization effects.

The structure was solved by a combination of Patterson and direct methods. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 2880 observed reflections (I > 3.00σ(I)) and 190 variable parameters and converged (largest parameter shift was 0.28 times its e.s.d.) with unweighted and weighted agreement factors of R = 0.043 and R$_w$ = 0.045. The standard deviation of an observation of unit weight was 1.37. Neutral atom scattering factors were taken from Cromer and Waber [24]. Anomalous dispersion effects were included in F$_{calc}$ [25]; the values of Δf' and Δf" were those of Cromer [26]. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corp. [27].

5. Supplementary material available

Final positional parameters and thermal parameters for $[Re(O^tBu)_2(CO)]_2(\mu\text{-}C^tBu)_2$ (4 pages) are available from the authors.

Acknowledgements

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