for $4.0 < 2\theta < 50.0°$ by Wyckoff ω scans. Three check reflections remeasured after every 100 ordinary data showed a decay of 4% and variation of 5% over the period of data collection, the latter apparently associated with intermittent buildup of ice around the crystal; an appropriate correction was therefore applied. Of the 6841 intensity data collected, 6251 unique observations remained after averaging of duplicate and equivalent measurements and deletion of systematic absences; of these, 5215 with $I > 2\sigma(I)$ were retained for use in structure solution and refinement. An absorption correction was applied on the basis of the indexed crystal faces; maximum and minimum transmission coefficients were 0.775 and 0.671, respectively. Lorentz and polarization corrections were applied. The structure was solved by conventional heavy-atom (Patterson and Fourier) methods. All non-hydrogen atoms were assigned anisotropic displacements and all hydrogen atoms fixed isotropic displacement parameters. All non-hydrogen atoms and the hydrogen atom H(1) were refined without positional constraints. All other hydrogen atoms were constrained to idealized geometries (C-H = 0.96 Å, H-C-H = 109.5°). One chlorine atom of the anion showed abnormally large displacement parameters as well as a uniquely short Cl-Al distance. Refinement of its occupancy revealed that this site was occupied approximately equally by carbon and chlorine atoms. Separation of the positions of carbon and chlorine atoms led to unstable refinement without identifying distinct positions for these atoms and was therefore abandoned. Accordingly, the atomic site composition was refined, giving final occupancies of 0.47 (1) and 0.53 (1) for the chlorine and carbon atoms at this position (Cl(8)). Full-matrix least-squares refinement of this model (371 parameters) converged to final residual indices $R = 0.053$, $R_w = 0.077$, and $S = 1.999$. Weights, w, were set equal to $[\sigma_c^2(F_o) + gF_o^2]^{-1}$, where $\sigma_c^2(F_o)$ is the variance in F_o due to counting statistics and $g = 0.0007$ was chosen to minimize the variation in S as a function of $|F_o|$. Final difference electron density maps showed no features outside the range +1.2 to −1.11 e Å^{-3}, the largest of these being close to the chlorine atoms of the anion. Attempts to model these electron density features led to physically unreasonable models. All calculations were carried out on a Nicolet R3m/V structure determination system using programs of the SHELXTL-PLUS package.[40] Complex neutral-atom scattering factors were taken from ref 41.

Supplementary Material Available: Listings of anisotropic displacement parameters and hydrogen atomic parameters for complex 1 (2 pages); a listing of observed and calculated structure factors for 1 (23 pages). Ordering information is given on any current masthead page.

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Synthetic, Structural, and Reactivity Studies of Dirhenium Carbonyl Complexes of 17α-Ethynylestradiol and Phenylacetylene: Variable-Temperature ^{13}C NMR Spectra and X-ray Crystal Structure of (μ-H)(μ-C≡C–R)$Re_2(CO)_7$(MeCN)

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$Re_2(CO)_9$(MeCN) and $Re_2(CO)_8(MeCN)_2$ have been investigated for the synthesis of dirhenium complexes of alkynes. Only $Re_2(CO)_8(MeCN)_2$ reacts with 17α-ethynylestradiol and phenylacetylene to produce the complexes (μ-H)(μ-C≡C—R)$Re_2(CO)_7$(MeCN) (1, R = α-ethynylestradiol; 2, R = Ph). Compound 1 was characterized by X-ray diffraction methods: space group $P2_1/n$, $Z = 4$, $a = 7.4262$ (7) Å, $b = 16.146$ (2) Å, $c = 17.060$ (3) Å, $\beta = 101.13$ (1)°. A total of 3301 reflections with $I > 3\sigma(I)$ were used to solve and refine the structure to $R = 0.023$ and $R_w = 0.025$ (258 least-squares parameters). 1 and 2 have been found to react with CO gas, pyridine, and PPh_3 by replacement of the MeCN ligand. The ^{13}C NMR spectra of the complexes (μ-H)(μ-C≡C—R)$Re_2(CO)_7$(L), where L = MeCN or pyridine, reveal a fluxional process involving the carbonyls at the metal bearing the L ligand; the triphenylphosphine compounds, L = PPh_3, do not exhibit this fluxionality. A barrier of 15.7 ± 0.4 kcal mol^{-1} was obtained for the fluxional process in compound 1. The apical CO in complex 3 or 6 is very labile; it can be easily substituted by MeCN, pyridine, PPh_3, and n-$PrNH_2$. The reaction with n-$PrNH_2$, leading to the formation of complexes (μ-H)(μ-C≡C—R)-$Re_2(CO)_7$(n-$PrNH_2$), may be contrasted with the behavior of related Fe, Ru, and Os alkyne complexes in which amines react as a nucleophile at the C_α and C_β acetylide carbons.

Introduction

Since the first report appeared in 1974 describing the use of amine oxides to remove coordinated carbon monoxide,[1] these reagents have proven to be very convenient for ligand substitution reactions on metal carbonyl complexes. For example, the substitution of carbon monoxide by the ligand acetonitrile, phosphine, or pyridine is achievable by using this method. Moreover, the reaction of aldehydes, ketones, amides, alkenes, or alkynes with metal carbonyls is improved by using acetonitrile com-

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(1) Shvo, V.; Hazum, E. *J. Chem. Soc., Chem. Commun.* **1974**, 336.

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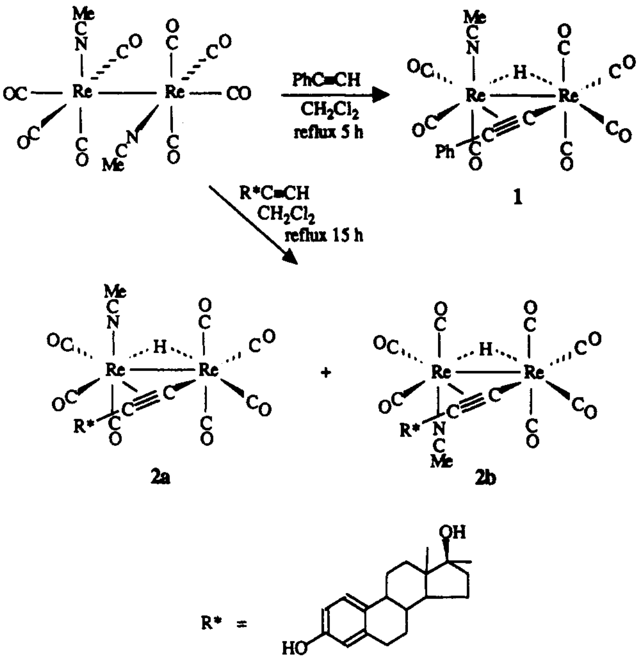
pounds, rather than by use of the amine oxide alone.[2] This success is understandable in terms of a combination of two factors: first, the acetonitrile ligand stabilizes the reactive intermediate M$_x$(CO)$_y$(MeCN)$_z$ which is formed by removing one or more of the CO groups in the metal carbonyl starting material by use of amine oxide, and secondly, the acetonitrile ligand is labile enough to be removed, thus allowing the ready incorporation of the desired functionality. While this method has been used for the syntheses of osmium and ruthenium complexes, we are unaware of any applications in the rhenium series. Despite the fact that Re$_2$(CO)$_9$(MeCN) and Re$_2$(CO)$_8$(MeCN)$_2$ have been known since 1978, only exchange reactions with phosphines or amines have been studied.[3] We thought it of interest to examine the reactivity of these acetonitrile rhenium compounds toward unsaturated ligands such as alkynes. The photochemical reaction of alkynes with Re$_2$(CO)$_{10}$ has been reported by Brown and co-workers and leads to the formation of complexes of the type (μ-H)(μ-C≡C—R)Re$_2$(CO)$_8$,[4] and we surmised that the use of Re$_2$(CO)$_9$(MeCN) and Re$_2$(CO)$_8$(MeCN)$_2$ could provide more convenient routes to such systems.

We have recently reported preliminary data on the reactivity of Re$_2$(CO)$_9$(MeCN) and Re$_2$(CO)$_8$(MeCN)$_2$ with α-ethynylestradiol and phenylacetylene, together with an X-ray crystallographic characterization of the phenyl derivative.[5] We now describe, in this paper, the full study on the syntheses and the reactivity of (μ-H)(μ-C≡C—R)Re$_2$(CO)$_7$L complexes (R = Ph, steroid; L = CO, MeCN, pyridine, PPh$_3$, and *i*-Pr). We also report a study of the fluxionality of some of these complexes by variable-temperature NMR experiments. One of the long-term goals of this project is the potential use of an α-ethynylestradiol–rhenium complex whereby the transition metal can function as a marker in a biological system.[6] We have already synthesized steroidal hormone complexes or Cr, Co, Mo, Os,[6a–c] Fe,[7] and Rh;[8] we wish to extend the range of such systems so as to take advantage of the potential use of isotopes such as ^{186}Re and ^{188}Re as radioactive therapeutic agents.[9]

Results and Discussion

Scheme I. Synthetic Routes to 1 and 2



Syntheses of Dirhenium Complexes of Phenylacetylene and 17β-Ethynylestradiol. The triple bond in α-ethynylestradiol has been shown to react readily with a number of transition-metal complexes. We have used this functionality to attach organometallic units such as Co$_2$(CO)$_6$, Cp$_2$Mo$_2$(CO)$_4$, or Os$_3$(CO)$_{10}$ onto the hormonal skeleton.[6a,c] It is known that alkynes react with Re$_2$(CO)$_{10}$ in both thermal and photochemical processes. However, the treatment of alkynes with Re$_2$(CO)$_{10}$ at 190 °C in an autoclave leads to the formation of rhenium complexes in which the alkyne is dimerized or tetramerized.[10] This method is not appropriate for the formation of rhenium–hormone complexes since it is only the monomer which is likely to be recognized by the receptor. As demonstrated by Brown et al.,[4] photolysis of Re$_2$(CO)$_{10}$ in the presence of an alkyne resulted in the formation of (μ-H)(μ-C≡C—R)Re$_2$(CO)$_8$. However, irradiation of a solution of 17α-ethynylestradiol and Re$_2$(CO)$_{10}$ in toluene gave low yields of a complex mixture, and so instead we turned to the amine oxide route mentioned above.

Me$_3$NO is a convenient reagent for removing CO ligands from transition-metal carbonyl compounds; in the presence of MeCN this provides a route to lightly-stabilized nitrile complexes from which the acetonitrile can subsequently be displaced by an appropriate ligand. For example, Os$_3$(CO)$_{10}$(MeCN)$_2$[2a–c] and Ru$_3$(CO)$_{10}$(MeCN)$_2$[2d] have been used to prepare complexes with alkynes, amides, or aldehydes. Although Koelle has prepared Re$_2$(CO)$_9$(MeCN) and Re$_2$(CO)$_8$(MeCN)$_2$, the only exchange reactions reported are those with phosphines and with pyridine.[3]

Initially, phenylacetylene and 17α-ethynylestradiol were each heated under reflux for 2 days with Re$_2$(CO)$_9$(MeCN) in dichloromethane, but IR data and chromatography revealed that the starting materials were essentially unchanged. It is clear that the monosubstituted complex Re$_2$(CO)$_9$(MeCN) is relatively inert toward reaction with the triple bond. In contrast, as shown in Scheme I, the reaction of phenylacetylene with Re$_2$(CO)$_8$(MeCN)$_2$ proceeds smoothly in refluxing dichloromethane over a 5-h period to give (μ-H)(μ-C≡CPh)Re$_2$(CO)$_7$(MeCN) (1) in 54% yield. The ^{1}H NMR, ^{13}C NMR, and IR spectroscopic data are summarized in Table I. Especially notable is the absorption at δ −11.5 which confirms the presence of the μ-H moiety. The MeCN ligand is characterized by methyl

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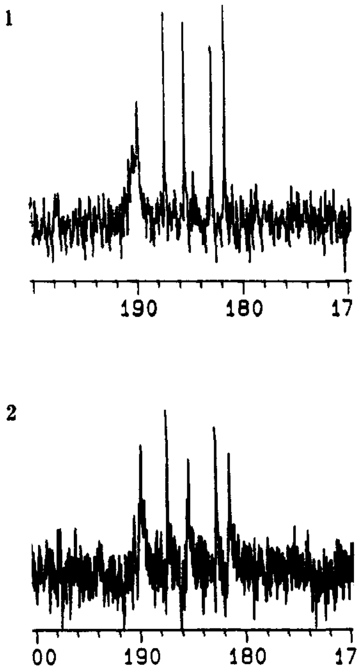

Figure 1. ^{13}C NMR spectra of 1 and 2 in the carbonyl region.

peaks at δ 2.20 and 3.29 in the ^1H and ^{13}C spectra, respectively; there is also a ^{13}CN resonance at 101.8 ppm. The ^{13}C NMR spectrum in the metal carbonyl region shows a large multiplet peak at 189.8 ppm and four sharp resonances at 187.3, 185.4, 182.8, and 181.5 ppm. The IR spectrum exhibits six ν_{CO} bands at 2100, 2034, 2000, 1987, 1955, and 1929 cm^{-1}, quite different from those of Brown's (μ-H)(μC≡CPh)$Re_2(CO)_8$ complex (which gives rise to ν_{CO} absorptions at 2119, 2094, 2023, 2002, and 1982 cm^{-1}).[4a] The structure of (μ-H)(μ-C≡CPh)$Re_2(CO)_7$(MeCN) (1) was subsequently confirmed by X-ray crystallography.

Likewise, when 17α-ethynylestradiol was heated with $Re_2(CO)_8(MeCN)_2$ under the same conditions, complex 2 was formed in good yield but the required reaction time was longer (15 h of reflux versus 5 h for the phenylacetylene complex). The ^1H and ^{13}C NMR chemical shift values of the MeCN, μ-H, and CO fragments in 2 are very similar to those of complex 1, but for certain protons and carbons the resonances are doubled. For example, μ-H is seen as two peaks (at −11.75 and −11.76 ppm); moreover, the methyl protons of the MeCN ligand give rise to two singlets (at δ 2.18 and δ 2.14). The CO region closely resembles that of 1 and shows a large peak at 189.8 ppm and four sharp peaks at 187.3, 185.3, 182.7, and 181.4 ppm. The IR spectrum exhibits ν_{CO} peaks at 2099, 2033, 1999, 1984, 1953, and 1925 cm^{-1}. Figures 1 and 2 show, respectively, the comparisons of the ^{13}C NMR and IR spectra of 1 to those of 2 in the CO region. It is clear that these two compounds have essentially identical structures.

The doubling of certain resonances in the ^1H and ^{13}C NMR spectra of 2 is readily accounted for in terms of the formation of two diastereomers, **2a** and **2b**, which arise as a consequence of the chirality of the steroid unit. The formation of this diastereomeric mixture is also reflected in the ^{13}C NMR spectrum of the steroidal moiety of 2 which reveals two singlets for both C≡C carbons and also for the carbons in the D ring of the steroidal skeleton.

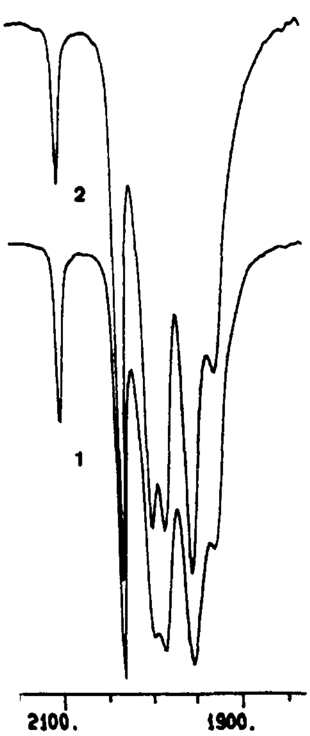

Figure 2. IR spectra of 1 and 2 in the carbonyl region (CH_2Cl_2).

It is now apparent that the reaction of an alkyne with dirhenium systems is greatly favored when the starting material contains not one but two lightly bonded ligands, such as acetonitrile. One can readily visualize initial loss of one MeCN moiety from diequatorial $Re_2(CO)_8(MeCN)_2$ to generate a coordinatively unsaturated center to which the alkyne can coordinate; in a subsequent step, loss of the second MeCN ligand and intramolecular oxidative addition of the acetylene C–H to the other rhenium can lead to (μ-H)(μ-C≡CPh)$Re_2(CO)_8$ (3) which reacts with liberated MeCN to yield the observed product 1. It has been hypothesized that the acetylide ligand is able to labilize the cis CO of octahedral complexes through stabilization of the coordinatively unsaturated transition-state species since it possesses two pairs of π electrons. One pair is involved in coordination while the other is available for π donation in the unsaturated transition state.[4a] Indeed, in an independent reaction, treatment of 3 with MeCN leads immediately to 1 (vide infra).

X-ray Crystal Structure of 1. (μ-H)(μ-C≡CPh)$Re_2(CO)_7$(MeCN) (1) crystallizes from CH_2Cl_2/pentane in the monoclinic space group $P2_1/n$. Crystallographic data, atomic coordinates, and bond lengths and angles are listed in Tables II–V. The molecular structure of 1 appears as in Figure 3 and is reminiscent of that of (μ-H)(μ-NC_6H_4)$Re_2(CO)_8$ previously reported by Brown.[11] The molecule possesses an eclipsed structure in contrast to the staggered orientation of the equatorial carbonyls in $Re_2(CO)_{10}$.[12] The Re–Re distance is 3.0788 Å, slightly longer than that of $Re_2(CO)_{10}$ (3.0413 Å)[13] but shorter than that found in (μ-H)(μ-NC_6H_4)$Re_2(CO)_8$ (3.2324 Å).[11] The MeCN ligand is perpendicular to the mean plane defined by Re(1), Re(2), C(3), and H(1); the C—N—Re angle is 178.5°. The phenylacetylido ligand is clearly bound to the two rhenium atoms in a μ-η^1,η^2 fashion. The Re(2)–C(4) is 2.446 Å, slightly longer than that of the Re(2)–C(3) bond (2.307 Å). The length of the C≡C triple bond (1.216 Å) is slightly longer than those of (μ-H)(μ^1-C≡CPh)$Re_2(CO)_7$(μ-dmpm) complex (1.200 Å)[4b] and free ligand acetylene (1.204 Å).[14] Overall, these results show little

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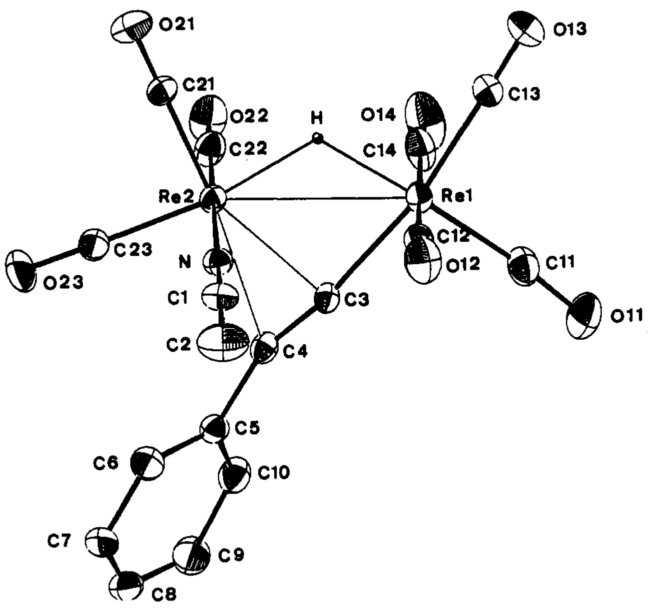
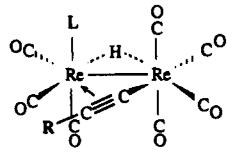


Figure 3. ORTEP drawing of (μ-H)(μ-C≡CPh)Re$_2$(CO)$_7$(MeCN) (**1**).

change in the Re–Re and C≡C bond lengths in **1** from those of the starting materials. However, we do see that the angle C(23)—Re(2)—Re(1) is about 13° larger than that of Re(2)—Re(1)—C(11), 157.6° versus 144.5°. This must arise as a consequence of the steric requirements of the bridging alkynyl moiety.

Reactivity and Fluxionality of 1 and 2. One might reasonably expect that the acetonitrile ligand in both **1** and **2** should be rather labile. Indeed, reaction with CO, pyridine, and triphenylphosphine proceeds readily to give complexes **3** through **8**. It is particularly noteworthy that **6** is chiral only by virtue of the steroidal substituent. The replacement of the MeCN by a CO ligand has removed the local asymmetry about the rhenium atom to which the alkyne is π-bonded. That is, the diastereomeric mixture **2a** and **2b** yields a single isomer **6** which no longer shows the doubling of the bridging hydride nor of the steroidal carbons. It is noteworthy that the MeCN ligand can be replaced by CO gas under mild conditions, viz., 70 °C under CO gas at atmospheric pressure.



1	R = Ph ;	L = MeCN	**2**	R = Steroid ;	L = MeCN
3	R = Ph ;	L = CO	**6**	R = Steroid ;	L = CO
4	R = Ph ;	L = Pyridine	**7**	R = Steroid ;	L = Pyridine
5	R = Ph ;	L = Ph$_3$P	**8**	R = Steroid ;	L = Ph$_3$P
9	R = Ph ;	L = n-PrNH$_2$	**10**	R = Steroid ;	L = n-PrNH$_2$

Before analyzing the NMR fluxionality of this series of molecules, one must first recall the data on (μ-H)(μ-C≡CPh)Re$_2$(CO)$_8$ (**3**) reported by Brown. The C_s symmetry found for **3** in the solid state would mandate a ^{13}CO NMR peak multiplicity of 1:1:2:1:1:2, but at room temperature, the ^{13}CO spectrum exhibits a 2:2:4 pattern consistent with effective C_{2v} symmetry. This behavior is rationalizable in terms of a rapid σ,π-acetylide interchange process, as in Scheme II. An activation energy of 11.3 kcal/mol has been reported by Carty for an analogous process in (μ-PPh$_2$)(μ-C≡C-*i*-Pr)Os$_2$(CO)$_6$.[15] Analogous alkenyl migrations have been described by Brown and have been found to exhibit a barrier of 12.7 kcal/mol.[16] Shapley et al. have observed this σ,π-alkenyl-interchange process on the trimetallic cluster HOs$_3$(CO)$_{10}$(CPh=CHPh), and a value of 11.3 kcal/mol has been measured for the activation energy.[17] In the related system (μ-H)(μ-C≡CH)Re$_2$(CO)$_6$(dppm), Brown has reported a barrier of 10.5 kcal/mol for the fluxionality of the acetylide ligand.[4b]

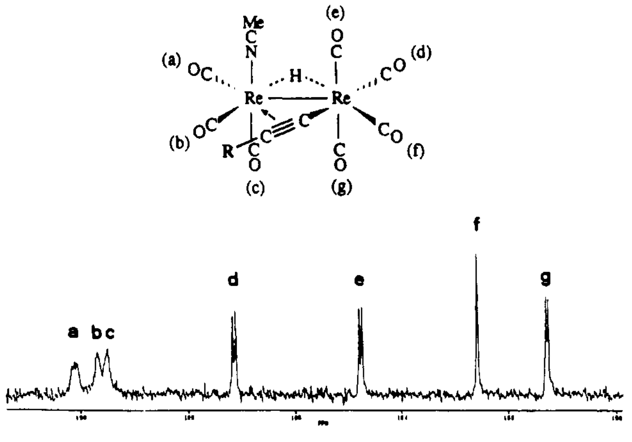
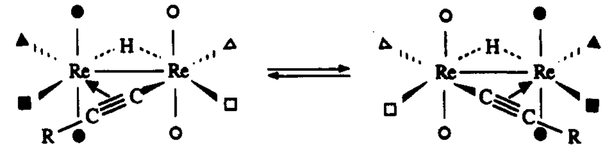
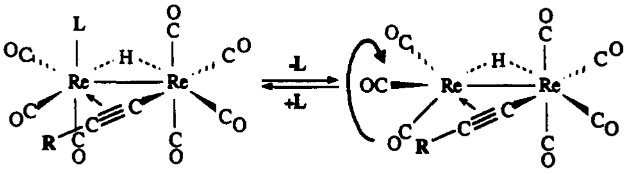


Figure 4. 62.9-MHz ^{13}C NMR spectrum of **1** at −40 °C. Assignments of carbonyls a–c are arbitrary.

Scheme II. σ,π-Acetylide Exchange Process



Scheme III. Proposed Mechanism To Account for the Fluxionality of 1



In such a σ,π interconversion were to occur in **1**, one should expect to see fourteen resonances rather than the seven carbonyl peaks actually observed at low temperature in the ^{13}C NMR spectrum (see Figure 4). One might suggest that the fluxional process is still rapid on the NMR time scale but such a proposal can be countered by noting the relative simplicity of the IR spectrum where we see only six ν_{CO} absorptions. It would appear, therefore, that changes in the variable-temperature ^{13}CO NMR spectra of **1** are not attributable to σ,π-acetylide-exchange process.

It is clear from Figure 5 that as the temperature is raised from −40 °C, there is a gradual merging of the three resonances at 190.09, 189.70, and 189.50 ppm; subsequently, there is another coalescence between the peaks at 185.4 and 181.5 ppm. Although the temperature ranges over which these coalescences occur are very different, this is merely a consequence of the very different chemical shift

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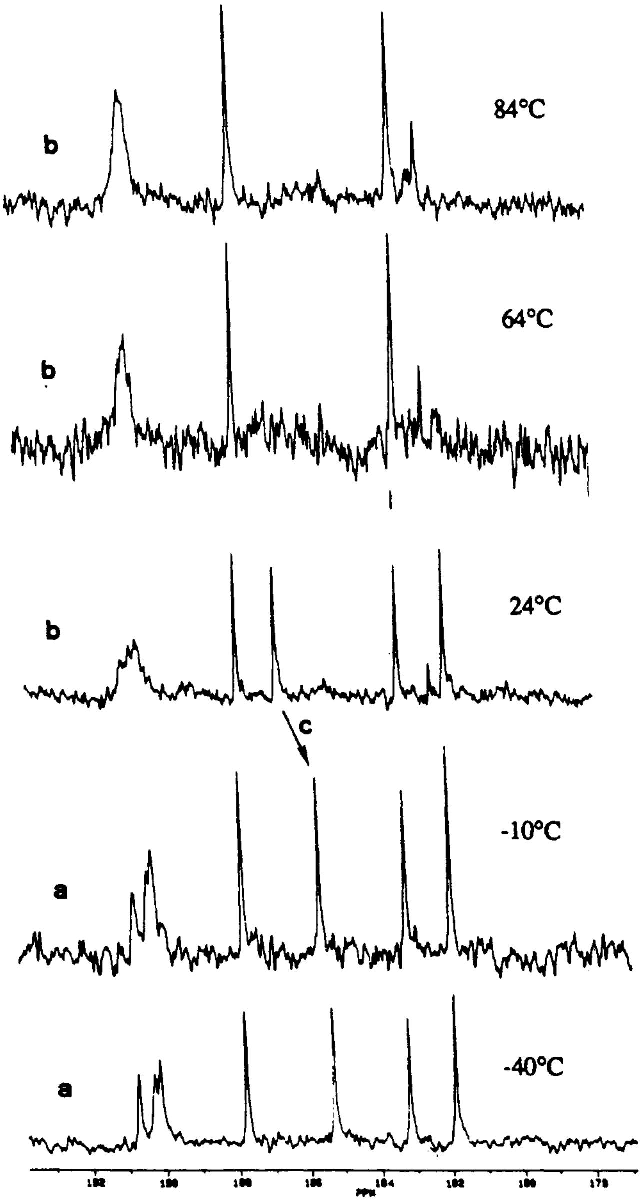

Figure 5. Variable-temperature ^{13}C NMR spectra of 1 in the CO region from +20 to −40 °C (a) in CD_2Cl_2 and (b) in toluene-d_8. (c) This change of δ value is attributable to the different solvents.

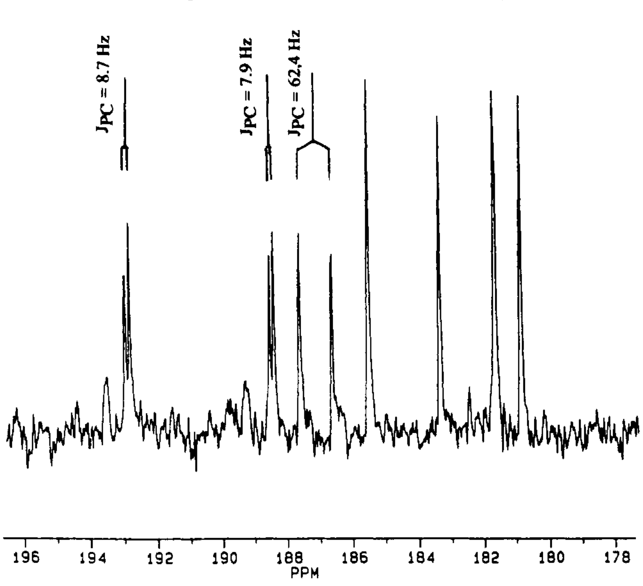

Figure 6. ^{13}C NMR spectrum of 5 is the carbonyl region.

separations and the calculated activation energies are the same within experimental error (15.7 ± 0.4 kcal/mol). One can thus conclude that these different coalescence phenomena are merely manifestations of the same fluxional process. Scheme III shows a straightforward rationale whereby loss of the acetonitrile ligand leaves one rhenium atom coordinatively unsaturated. Rapid interconversion of the a, b, and c carbonyls generates a molecule of effective C_s symmetry; this has the effect of equilibrating the e and g environments which lie on opposite sides of the molecular mirror plane. This scrambling process on one $M(CO)_3$ unit leaving static the other metal unit has been observed for (μ-PPh_2)(μ-C≡C-*i*-Pr)$Fe_2(CO)_6$,[15] [μ-C{NHR}CH(Ph)][(μ-PPh_2)$Fe_2(CO)_6$,[18] and [μ_2-η^2-CH=C=CPh)(μ-PPh_2)$Ru_2(CO)_6$.[19] This result raises an interesting point concerning the assignments of the four carbonyls on the rhenium to which the acetylide is σ-bonded. Brown had earlier suggested that in 3 the carbonyls positioned trans to the bridging hydrogen exhibit a J_{C-H} value of ca. 3.5 Hz.[4a] We see in Figure 4 that peaks d, e, and g show small J_{C-H} couplings with f is a sharp singlet. Clearly, carbonyls e and g (which are equilibrated during the fluxional process) must be oriented cis to the bridging hydrogen. Furthermore, we see from the X-ray crystal structure of 1 that three of these carbonyl groups make H—Re—CO angles of 90 ± 3° while for the remaining carbonyl ligand this angle is 176°. One is tempted to assign the singlet resonance at 182.8 ppm to the carbonyl in position f, thus leaving all three cis ligands as proton-coupled doublets. This proposal gains extra support from the observation that the Re—*C*≡CPh alkynyl carbon at 101.8 ppm, which is certainly cis to the bridging hydrogen atom, is also a doublet (J_{C-H} = 4 Hz) in the proton-coupled ^{13}C spectrum. The other alkynyl carbon, viz. Re—C≡*C*Ph at 98.9 ppm, exhibits a 5-Hz triplet pattern, presumably attributable to coupling with the ortho hydrogens of the phenyl ring.

The analogous pyridine complex, 4, behaves similarly to 1. The same fluxional process may be invoked, and again, the rate-determining step would appear to be the loss of the weakly bonded pyridine ligand. A comparison of the ^{13}C spectra of 1 and 4 in the carbonyl region reveals that the only significant difference in chemical shift is found for the e resonances (185.4 ppm in 1 versus 183.5 in 4), and we assign each of these as the carbonyl in the same plane as the nitrogen donor ligand. We have in all cases attributed all three carbonyls at highest frequency (lowest field) as those bonded to the same rhenium as the ligand L. This is readily confirmed by the spectrum of the triphenylphosphine derivatives 5 and 8, as shown in Figure 6. In these cases, each of these deshielded ^{13}C resonances shows clear coupling to the neighboring phosphorus-31 nucleus. We follow the normal practice in that the largest J_{C-P} value is assigned to the trans carbonyl; in this case, there is no ambiguity; two of the CO's exhibit J_{C-P} values of 8 Hz while for the third carbonyl the value is 62 Hz. The crucial observation for both 5 and 8 is that there is no fluxionality of the carbonyls in these molecules. Clearly, the fact that the Ph_3P ligand is known to be able to bind firmly to the rhenium center engenders some confidence in our assertion that the fluxional process requires cleavage of a weak bond such as that between rhenium and acetonitrile or pyridine.

Reactivity of 3 and 6. The high lability of an apical CO of 3 was first noticed by Brown et al.[4a] The first-order

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Table I. Spectroscopic Data

complex	IR ν_{CO},[a] $\nu_{C\equiv C}$,[b] cm^{-1}	^{1}H NMR,[c] δ	^{13}C,[c] δ
1	2100 (w), 2034 (s), 2000 (s), 1987 (sh), 1955 (s), 1929 (sh)	7.56 (dd, 2 H, Ph$_o$), 7.45 (m, 1 H, Ph$_p$), 7.39 (m, 2 H, Ph$_m$), 2.20 (s, 3 H, Me), −11.45 (s, μ-H)	189.84 (m, 3 CO), 187.27 (1 CO), 185.38 (1 CO), 182.75 (1 CO), 181.54 (1 CO), 131.75 (Ph$_m$), 128.80 (Ph$_{ip}$), 128.71 (Ph$_o$), 128.35 (Ph$_p$), 119.63 (CN), 101.78 (C≡), 98.85 (≡C—Ph), 3.29 (Me)
2	2099 (w), 2033 (s), 1999 (s), 1984 (s, sh), 1953 (s), 1925 (m, sh)	7.20 (d, 1 H, H(1)), 6.61 (dd, 1 H, H(2)), 6.56 (d, 1 H, H(4)), 5.38 and 5.08 (s, s, OH), 2.83 (m, 2 H, H(6)), 2.18 and 2.14 (s, s, 3 H, MeCN), 1.05 (s, 3 H, Me-13), −11.75 and −11.76 (s, s, 1 H, μ-H)	189.75 (m, 3 CO), 187.27 (1 CO), 185.26 (1 CO), 182.65 (1 CO), 181.42 (1 CO), 153.67 (C(3)), 138.60 and 138.42 (C(5)), 132.78 (C(10)), 126.67 (C(1)), 119.37 (CN), 115.25 (C(4)), 112.69 (C(2)), 109.84, 109.44, 98.55, 98.14 (C≡C), 84.90 and 84.65 (C(17)), 49.57, 49.25 and 49.00 (C(13) and C(14)), 44.13 (C(9)), 40.34 and 39.44 (C(16)), 39.96 (C(8)), 33.44 and 33.32 (C(12)), 29.78 (C(6)), 27.52 (C(7)), 26.98 (C(11)), 23.26 and 23.07 (C(15)), 14.32 and 14.20 (Me-13), 3.38 and 3.17 (MeCN)
3[d]	2117 (w), 2092 (m), 2020 (s), 1997 (s), 1970 (s)	7.56 (dd, 2 H, Ph$_o$), 7.43 (m, 3 H, Ph$_p$ and Ph$_m$), −13.01 (s, 1 H, μ-H)	184.96 (2 CO), 182.45 (2 CO), 181.69 (4 CO), 132.35 (Ph$_m$), 129.21 (Ph$_p$), 129.07 (Ph$_o$), 89.07, 88.46 (C≡C)
4[d]	2101 (w), 2028 (s), 1955 (s), 1955 (s), 1934 (s), 1919 (s, sh)	8.47 (dd, 2 H, Py$_o$), 7.73 (m, 1 H, Py$_p$), 7.25 (dd, 2 H, Py$_m$), 7.73 (dd, 2 H, Ph$_o$), 7.46 (dd + t, 3 H, Ph$_m$ + Ph$_p$), −10.42 (s, 1 H, μ-H)	193.16 (m, 3 CO), 187.28 (1 CO), 183.48 (1 CO), 182.90 (1 CO), 181.39 (1 CO), 153.93 (Py$_o$), 138.84 (Py$_p$), 132.22 (Ph$_m$), 129.09 (Ph$_o$), 128.58 (Ph$_p$), 128.20 (Ph$_{ip}$), 126.13 (Py$_m$), 109.11, 103.21 (C≡C)
5	2104 (w), 2029 (s), 2009 (s), 1996 (s, sh), 1961 (s), 1927 (s)	7.44 (m, Ph + PPh$_3$), −11.98 (d, μ-H, J_{HP} = 8.5 Hz)	192.87 (d, 1 CO, J_{PC} = 8.7 Hz), 188.42 (d, 1 CO, J_{PC} = 7.9 Hz), 187.08 (d, 1 CO, J_{PC} = 62.4 Hz), 185.46 (1 CO), 183.31 (1 CO), 181.63 (1 CO), 180.81 (1 CO), 134.61 (d, Ph$_o$, J_{PC} = 10.9 Hz), 130.76 (s, Ph$_p$ (P)), 128.67 (s, Ph$_m$ (P)), 131.97 (Ph$_m$), 128.50 (Ph$_o$), 128.35 (Ph$_p$), 100.83 (C≡, J_{CH} = 9.0 Hz), 89.74 (C≡)
6	2119 (w), 2092 (m), 2019 (s), 1998 (s), 1970 (s)	7.19 (d, 1 H, H(1)), 6.61 (dd, 1 H, H(2)), 6.55 (d, 1 H, H(4)), 5.03 (s, OH), 2.82 (m, 2 H, H(6)), 1.04 (s, 3 H, Me-13), −13.36 (s, s, 1 H, μ-H)	184.82 (2 CO), 282.23 (2 CO), 181.58 (2 CO), 181.35 (1 CO), 153.65 (C(3)), 138.54 (C(5)), 132.70 (C(10)), 126.73 (C(1)), 115.28 (C(4)), 112.77 (C(2)), 99.65, 86.00 (C≡C), 84.57 (C(17)), 49.51 (C(14)), 48.98 (C(13)), 44.07 (C(9)), 40.43 (C(8)), 39.94 (C(16)), 33.52 (C(12)), 29.77 (C(6)), 27.50 (C(7)), 26.91 (C(11)), 23.11 (C(15)), 14.25 (Me-13)
7	2099 (w), 2028 (s), 1993 (s), 1990 (s, sh), 1953 (s), 1927 (m), 1917 (s, sh)	8.74 and 8.67 (d and m, 2 H, Py$_o$), 7.72 (m, 1 H, Py$_p$), 7.20 (m, 3 H, Py$_m$ + H(1)), 6.62 (dd, 1 H, H(2)), 6.56 (d, 1 H, H(4)), 5.32 (br, OH), 2.84 (m, 2 H, H(6)), 1.13 (s, 3 H, Me-13), −10.72 (s, 1 H, μ-H)	193.07 (m, 3 CO), 187.38 (1 CO), 183.33 (1 CO), 182.95 (1 CO), 181.56 (1 CO), 155.30 and 154.79 (Py$_o$), 138.68 and 138.46 (Py$_p$), 125.81 and 125.57 (Py$_m$), 153.89 (C(3)), 137.73 (C(5)), 132.99 (C(10)), 126.73, (C(1)), 115.43 (C(4)), 112.89 (C(2)), 112.52, 105.09 (C≡C), 85.79 (C(17)), 49.42 (C(14)), 49.23 (C(13)), 44.35 (C(9)), 41.41 (C(8)), 40.23 (C(16)), 33.43 (C(12)), 29.86 (C(6)), 27.72 (C(7)), 27.10 (C(11)), 23.17 (C(15)), 14.37 and 14.08 (Me-13)
8	2101 (w), 2028 (s), 2011 (s), 1999 (s, sh), 1959 (s), 1928 (s)	7.43 (m, 15 H, PPh$_3$), 7.18 (d, 1 H, H(1)), 6.61 (dd, 1 H, H(2)), 6.56 (d, 1 H, H(4)), 5.45 (br, OH), 2.86 (m, 2 H, H(6)), 1.09 and 1.02 (s, 3 H, Me-13), −12.25 (d, 1 H, μ-H, J_{HP} = 9 Hz)	192.32 and 191.93 (d, d, 1 CO, J_{PC} = 8.7 Hz and 7.4 Hz), 188.98 and 188.46 (d, d, 1 CO, J_{PC} = 6.5 Hz and 8.3 Hz), 186.86 and 186.73 (d, d, 1 CO, J_{PC} = 62.3 Hz and 66.3 Hz), 185.82 and 185.40 (s, s, 1 CO), 183.27 and 182.80 (s, s, 1 CO, 181.59 and 181.30 (s, s, 1 CO), 181.52 and 181.86 (s, s, 1 CO), 153.82 (C(3)), 138.39 (C(5)), 134.46 (d, Ph$_o$, J_{PC} = 11.1 Hz), 130.77 (s, Ph$_p$), 128.64 (s, Ph$_m$), 132.45 (C(10)), 126.75 and 126.64 (C(1)), 115.28 and 115.27 (C(4)), 112.81 and 112.75 (C(2)), 102.13 and 101.89 (d, d, C≡, J_{PC} = 1.6 Hz and 1.6 Hz), 95.35 and 94.53 (d, d, C≡, J_{PC} = 8.7 Hz and 6.4 Hz), 84.61 and 84.51 (C(17)), 49.55 and 49.52 (C(14)), 49.16 (C(13)), 44.15 and 44.05 (C(9)), 40.59 and 39.73 (C(16)), 40.00 and 39.94 (C(8)), 33.93 and 33.72 (C(12)), 29.91 and 29.78 (C(6)), 27.74 and 27.56 (C(7)), 27.05 (C(11)), 23.39 and 22.82 (C(15)), 14.42 and 14.24 (Me-13)
9	2100 (w), 2028 (s), 1976 (s), 1966 (s, sh), 1932 (s), 1919 (s, sh)	7.53 (d, 2 H, Ph), 7.39 (m, 3 H, Ph), 2.66 (m, 2 H, $\underline{CH_2}$-NH$_2$), 1.37 (m, 2 H, CH$_2$), 0.84 (t, 3 H, CH$_3$), 1.75 (s, 2 H, NH$_2$), −11.36 (s, 1 H, μ-H)	189.84 (m, 3 CO), 186.13 (1 CO), 185.61 (1 CO), 181.60 (1 CO), 181.10 (1 CO), 128.39 (Ph$_o$), 131.15 (Ph$_m$), 128.07 (Ph$_p$), 127.91 (Ph$_{ip}$), 104.87, 102.53 (C≡C); iPr 52.66 (CH$_2$—NH$_2$), 25.99 (CH$_2$), 9.96 (CH$_3$)

Table I (Continued)

complex	IR ν_{CO},[a] $\nu_{C≡C}$,[b] cm^{-1}	^1H NMR,[c] δ	^{13}C,[c] δ
10	2099 (w), 2026 (s), 2005 (s), 1976 (s), 1961 (s, sh), 1930 (s), 1914 (s, sh)	7.17 (d, 1 H, H1), 6.59 (dd, 1 H, H2), 6.53 (d, 1 H, H4), 2.80 (m, 2 H, $\underline{CH_2}$-NH_2), 1.35 (m, 2 H, $\underline{CH_2}$-CH_2-NH_2), 0.79 (t, 3 H, CH_3), 1.02 (s, 3 H, Me-13), −11.68 (s, 1 H, μ-H)	191.57 (m, 3 CO), 186.37 (1 CO), 185.31 (1 CO), 181.63 (1 CO), 179.89 (1 CO), 153.74 (C(3)), 137.93 and 137.80 (C(5)), 131.75 (C(10)), 126.11 (C(1)), 114.90 (C(4)), 112.38 (C(2)), 111.53, 100.09 (C≡C), 85.20 (C(17)), 48.43 and 48.23 (C(13) and C(14)), 43.54 (C(9)), 40.32 (C(16)), 39.59 (C(8)), 33.02 (C(12)), 29.31 (C(6)), 26.97 (C(7)), 26.42 (C(11)), 22.76 (C(15)), 13.65 (Me-13); iPr 51.92 ($\underline{CH_2}$—NH_2), 26.08 (CH_2), 9.98 (CH_3)

[a] CH_2Cl_2 solution. [b] $\nu_{C≡C}$ cannot be assigned by its overlap with ν_{CO}. [c] CD_2Cl_2 solution. [d] 3 and 4 have been prepared by Brown et al.; only IR and ^1H NMR data were known.[4a]

Table II. Summary of Crystallographic Data for (μ-H)(μ-C≡CPh)$Re_2(CO)_7$(MeCN) (1)

chem formula	$Re_2C_{17}H_9O_7N$
fw	711.66
cryst syst	monoclinic
space group	$p2_1/n$
Z	4
a, Å	7.2462 (7)
b, Å	16.146 (2)
c, Å	17.060 (3)
β, deg	101.13 (1)
V, Å^3	1958
$F(000)$	1296
ρ(calcd), g cm^{-3}	2.41
μ(Mo Kα), cm^{-1}	125.57
cryst size, mm	0.17 × 0.23 × 0.4
diffractometer	CAD4
monochromator	graphite
radiation; λ, Å	Mo Kα; 0.710 70
temp, °C	20
scan type	$\omega/2\theta$
scan range θ, deg	1.2 + 0.34 tan θ
2θ range, deg	2–56
no. of reflctn collcd	4723
no. of reflctn used (criteria)	3301 ($I > 3\sigma(I)$)
R	0.023
R_w[a]	0.025
abs corr[b]	min 0.79; max 1.38
secondary extinction	33.3 × 10^6
weighting scheme	unit weights
rms (shift/esd)	0.12
no. of least-squares params	258
residual electron density, e Å^{-3}	0.6

[a] $R_w = [\sum_i W_i(F_o - F_c)^2/\sum_i W_i F_o^2]^{1/2}$. [b] Difabs: Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 159.

Table III. Fractional Coordinates of (μ-H)(μ-C≡CPh)$Re_2(CO)_7$(MeCN) (1)

atom	x/a	y/b	z/c	U(eq), Å^2	U(iso), Å^2
Re(1)	0.16946 (4)	0.15804 (2)	0.00431 (2)	0.0478	
Re(2)	0.42188 (4)	0.26862 (2)	0.12772 (2)	0.0415	
N(1)	0.3193 (7)	0.2024 (3)	0.2200 (3)	0.0453	
C(1)	0.263 (1)	0.1694 (5)	0.2683 (4)	0.0546	
C(2)	0.191 (2)	0.1261 (8)	0.3317 (7)	0.0837	
C(3)	0.1123 (9)	0.2670 (4)	0.0619 (4)	0.0432	
C(4)	0.1059 (9)	0.3285 (4)	0.1024 (4)	0.0453	
C(5)	0.0308 (9)	0.3995 (4)	0.1379 (4)	0.0472	
C(6)	0.059 (1)	0.4117 (6)	0.2193 (5)	0.0661	
C(7)	−0.020 (1)	0.4763 (7)	0.2522 (6)	0.0723	
C(8)	−0.126 (1)	0.5317 (6)	0.2026 (7)	0.0774	
C(9)	−0.156 (1)	0.5231 (6)	0.1220 (7)	0.0830	
C(10)	−0.077 (1)	0.4573 (5)	0.0892 (5)	0.0634	
C(11)	−0.075 (1)	0.1439 (5)	−0.0554 (5)	0.0676	
O(11)	−0.234 (1)	0.1398 (5)	−0.0896 (4)	0.0997	
C(12)	0.107 (1)	0.0896 (5)	0.0930 (5)	0.0556	
O(12)	0.074 (1)	0.0465 (4)	0.1404 (4)	0.0791	
C(13)	0.268 (1)	0.0589 (5)	−0.0402 (5)	0.0614	
O(13)	0.328 (1)	0.0012 (4)	−0.0649 (4)	0.0850	
C(14)	0.240 (1)	0.2213 (6)	−0.0837 (5)	0.0701	
O(14)	0.276 (1)	0.2554 (5)	−0.1371 (4)	0.1010	
C(21)	0.6694 (9)	0.2250 (5)	0.1604 (4)	0.0509	
O(21)	0.8174 (8)	0.1987 (4)	0.1802 (4)	0.0754	
C(22)	0.501 (1)	0.3298 (5)	0.0452 (4)	0.0572	
O(22)	0.5491 (9)	0.3666 (4)	−0.0045 (3)	0.0751	
C(23)	0.488 (1)	0.3602 (5)	0.1987 (4)	0.0580	
O(23)	0.531 (1)	0.4132 (4)	0.2428 (4)	0.0806	
H(1)	0.38 (1)	0.173 (6)	0.061 (6)		0.13 (2)
H(21)	0.24 (1)	0.065 (7)	0.333 (6)		0.13 (2)
H(22)	0.17 (2)	0.154 (7)	0.378 (7)		0.13 (2)
H(23)	0.04 (2)	0.110 (7)	0.314 (6)		0.13 (2)

Table IV. Interatomic Distances (Å) of (μ-H)(μ-C≡CPh)$Re_2(CO)_7$(MeCN) (1)

Re(1)–Re(2)	3.0788 (4)	Re(2)–H(1)	1.9 (1)
Re(1)–H(1)	1.6 (1)	Re(2)–C(3)	2.307 (6)
Re(1)–C(3)	2.095 (7)	Re(2)–C(4)	2.446 (7)
Re(1)–C(11)	1.881 (9)	Re(2)–C(21)	1.907 (7)
Re(1)–C(12)	1.995 (8)	Re(2)–C(22)	1.897 (7)
Re(1)–C(13)	1.966 (8)	Re(2)–C(23)	1.913 (8)
Re(1)–C(14)	1.963 (9)	Re(2)–N(1)	2.151 (5)
N(1)–C(1)	1.121 (8)	C(1)–C(2)	1.47 (1)
C(3)–C(4)	1.216 (9)	C(4)–C(5)	1.450 (9)
C(5)–C(6)	1.38 (1)	C(5)–C(10)	1.39 (1)
C(6)–C(7)	1.36 (1)	C(7)–C(8)	1.36 (1)
C(8)–C(9)	1.36 (1)	C(9)–C(10)	1.38 (1)
C(11)–O(11)	1.19 (1)	C(21)–O(21)	1.142 (8)
C(12)–O(12)	1.128 (9)	C(22)–O(22)	1.144 (8)
C(13)–O(13)	1.139 (9)	C(23)–O(23)	1.142 (9)
C(14)–O(14)	1.14 (1)		

rate constant for the reaction of 3 with pyridine was found to be 4.9 × 10^{-4} s^{-1} at 26 °C. This lability has been attributed to the effect of the acetylide ligand which possesses two pairs of p_π electrons. We observed the same lability of this carbonyl for the bulky hormone complex 6; upon addition of pyridine or PPh_3 to the solution of 6, compounds 7 and 8 were formed in quantitative yield, as shown by use of IR spectroscopy. When MeCN was added to a solution of 3 or 6, we observed a slow exchange between CO and MeCN. Complexes 1 and 2 were finally obtained within 1 h. These reactions demonstrate the remarkably lability of the apical CO of acetylide rhenium complexes and should work with other π-donor ligands.

Such edge-bridged μ_2-η^2-acetylide complexes have been found to react with nitrogen- or carbon-based nucleophiles.[18,20,21] In the case of (μ-PPh_2)(μ-C≡CR)$M_2(CO)_6$, where M = Fe, Ru, or Os, the nucleophile can add at the β-carbon of the acetylide to form a one-carbon bridged product or at the acetylide α-carbon atom to form a two-carbon bridge complex (Scheme IV).[18]

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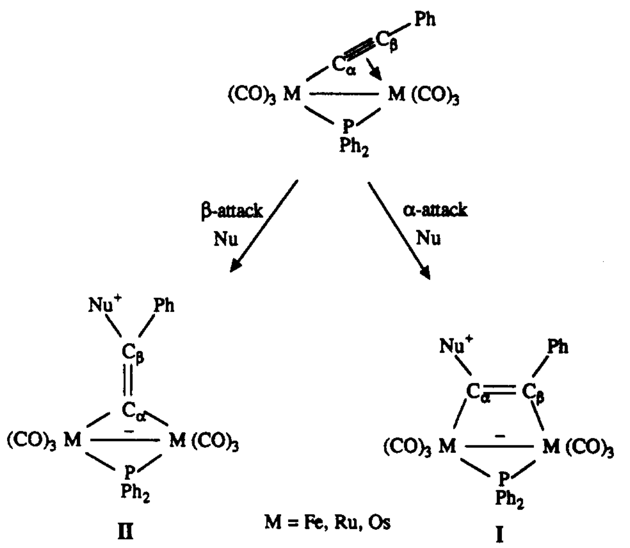
Table V. Bond Angles (deg) of $(\mu\text{-H})(\mu\text{-C}{\equiv}\text{CPh})\text{Re}_2(\text{CO})_7(\text{MeCN})$ (1)

C(3)–Re(1)–Re(2)	48.5 (2)	C(11)–Re(1)–Re(2)	144.5 (3)
C(11)–Re(1)–C(3)	96.0 (3)	C(12)–Re(1)–Re(2)	89.7 (2)
C(12)–Re(1)–C(3)	90.8 (3)	C(12)–Re(1)–C(11)	90.9 (4)
C(13)–Re(1)–Re(2)	121.6 (2)	C(13)–Re(1)–C(3)	170.1 (3)
C(13)–Re(1)–C(11)	93.9 (3)	C(13)–Re(1)–C(12)	89.7 (3)
C(14)–Re(1)–Re(2)	90.8 (2)	C(14)–Re(1)–C(3)	91.5 (3)
C(14)–Re(1)–C(11)	90.3 (4)	C(14)–Re(1)–C(12)	177.2 (4)
C(14)–Re(1)–C(13)	87.7 (4)	H(1)–Re(1)–Re(2)	32.2 (35)
H(1)–Re(1)–C(3)	80.6 (35)	H(1)–Re(1)–C(11)	176.0 (34)
H(1)–Re(1)–C(12)	87.1 (35)	H(1)–Re(1)–C(13)	89.5 (35)
H(1)–Re(1)–C(14)	91.9 (35)	N(1)–Re(2)–Re(1)	88.2 (1)
C(3)–Re(2)–Re(1)	42.9 (2)	C(3)–Re(2)–N(1)	84.8 (2)
C(21)–Re(2)–Re(1)	112.8 (2)	C(21)–Re(2)–N(1)	92.4 (2)
C(21)–Re(2)–C(3)	155.4 (3)	C(22)–Re(2)–Re(1)	91.1 (2)
C(22)–Re(2)–N(1)	177.1 (3)	C(22)–Re(2)–C(3)	92.8 (3)
C(22)–Re(2)–C(21)	90.5 (3)	C(23)–Re(2)–Re(1)	157.6 (2)
C(23)–Re(2)–N(1)	90.0 (3)	C(23)–Re(2)–C(3)	114.7 (3)
C(23)–Re(2)–C(21)	89.6 (3)	C(23)–Re(2)–C(22)	89.6 (3)
H(1)–Re(2)–Re(1)	27.4 (31)	H(1)–Re(2)–N(1)	89.4 (30)
H(1)–Re(2)–C(3)	70.2 (31)	H(1)–Re(2)–C(21)	85.3 (31)
H(1)–Re(2)–C(22)	91.2 (30)	H(1)–Re(2)–C(23)	174.9 (31)
C(1)–N(1)–Re(2)	178.5 (6)	C(2)–C(1)–N(1)	179.8 (9)
Re(2)–C(3)–Re(1)	88.6 (2)	C(4)–C(3)–Re(1)	170.1 (6)
C(4)–C(3)–Re(2)	81.6 (4)	C(5)–C(4)–C(3)	160.3 (7)
C(6)–C(5)–C(4)	122.7 (7)	C(10)–C(5)–C(4)	119.7 (7)
C(10)–C(5)–C(6)	117.6 (7)	C(7)–C(6)–C(5)	122.3 (9)
C(8)–C(7)–C(6)	118.6 (9)	C(9)–C(8)–C(7)	121.5 (9)
C(10)–C(9)–C(8)	119.5 (9)	C(9)–C(10)–C(5)	120.4 (8)
O(11)–C(11)–Re(1)	174.9 (8)	O(12)–C(12)–Re(1)	175.5 (7)
O(13)–C(13)–Re(1)	178.9 (8)	O(14)–C(14)–Re(1)	176.9 (8)
O(21)–C(21)–Re(2)	179.7 (7)	O(22)–C(22)–Re(2)	179.7 (7)
O(23)–C(23)–Re(2)	177.7 (8)	Re(2)–H(1)–Re(1)	120.4 (57)

Scheme IV



In order to examine the reaction of an amine with dirhenium complexes, we have allowed the primary amine n-PrNH$_2$ to react with 3 and 6. n-PrNH$_2$ reacts rapidly with 3 and 6 to give quantitative yields of $(\mu\text{-H})(\mu\text{-C}{\equiv}\text{C—R})\text{Re}_2(\text{CO})_7(n\text{-PrNH}_2)$, where R = Ph (9) and α-ethynylestradiol (10), respectively. The IR spectra of 9 (10) exhibit ν_{CO} peaks at 2100 (2099), 2028 (2026), 2008 (2005), 1976 (1976), 1966 (1966), 1932 (1930), and 1919 (1914) cm^{-1} showing that both 9 and 10 contain the same metal carbonyl unit. Compound I (Scheme III) is characterized by ^{13}C NMR peaks for C$_\alpha$ at 234.3 and for C$_\beta$ at 44.9 ppm (M = Fe); compound II exhibits peaks for C$_\alpha$ at 78.7 and for C$_\beta$ at 201.2 ppm.[18] The spectra of 9 and 10 did not show such peaks. Except for the peaks attributable to the amine, the remaining protons and carbons have δ values similar to those of 3–8. The acetylide carbons, C≡C, resonate at 104.87 and 102.53 ppm for 9 and at 111.53 and 100.09 ppm for 10. As was found for complexes 3–7, the carbonyl peaks of 9 and 10 exhibit one broad peak and four sharp peaks, as expected for fluxional molecules. These results show clearly that the structures of 9 and 10 are similar to those of 3–8 and result from the substitution of the apical CO by n-PrNH$_2$. We suggest that the difference in reactivity between Re complexes and Fe, Ru, and Os complex systems is attributable to the exceptional lability of the apical CO of rhenium complexes.

We have undertaken an investigation concerning the possibility of using a rhenium-containing moiety as a marker for hormones as we have already done for the metals Cr, Co, and Mo.[6] The recognition of modified hormones by their specific receptor is quantified by the measurement of the relative binding affinity (RBA). All hormone rhenium complexes described in this work gave an RBA value of zero. A plausible explanation of this result may be the high reactivity of rhenium complexes toward donor ligands, as shown in this work. The hormone complexes could react with many functional groups on the protein chains of the receptor, especially the amine function. This could prevent the hormone complexes from reaching the binding sites. However, this high reactivity of rhenium complexes could be exploited to mark peptides with radioactive rhenium isotopes. This interesting subject will be the topic of a forthcoming publication.

Conclusion

To summarize, therefore, the reaction of diequatorial $\text{Re}_2(\text{CO})_8(\text{MeCN})_2$ with terminal alkynes leads not to the expected product $(\mu\text{-H})(\mu\text{-C}{\equiv}\text{CPh})\text{Re}_2(\text{CO})_8$ (3) but instead to the acetonitrile-containing molecule $(\mu\text{-H})(\mu\text{-C}{\equiv}\text{CPh})\text{Re}_2(\text{CO})_7(\text{MeCN})$ (1), which has been characterized crystallographically. Both this system and its steroidal analogue 2, in which the phenyl group has been replaced by an estradiol moiety, exhibit ready replacement of the acetonitrile ligand by either pyridine or triphenylphosphine. The fluxional behavior of the acetonitrile and pyridine complexes is not observed for the phosphine systems, and this is rationalized in terms of a mechanism involving cleavage of the relatively weak bond between the rhenium and the nitrogen donor ligand. A primary amine reacts with rhenium complexes to substitute for an apical CO and not as a nucleophile on acetylide carbons as has been observed before on Fe, Ru, and Os complexes. It would be interesting to treat an amine with a complex that has already lost the labile CO such as 1, 4, or 5 to investigate the possibility of nucleophile attack by an amine.

Experimental Section

General Procedures. All reactions were performed under a dry argon atmosphere by using standard Schlenk techniques. $\text{Re}_2(\text{CO})_{10}$ was purchased from Strem Co.; other reagents and solvents were available from Aldrich Chemical Co. and Janssen Chemica Co. CH$_2$Cl$_2$ was distilled from CaH$_2$, MeCN was distilled from P$_2$O$_5$, and benzene and toluene were distilled from Na/Ph$_2$CO. Me$_3$NO·2H$_2$O was dehydrated by the published procedure.[22] The thin-layer chromatography technique was used to purify complexes by using silica gel plates under an air atmosphere; the eluants used were commercial grade without any purification. IR spectra were recorded on a Bomem Michelson 100 spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM-250 spectrometer operating at 250 MHz for ^{1}H and 62.9 MHz for ^{13}C. Mass spectra were obtained by the "Service de Spectrometrie de masse" of ENSCP, Paris, and CNRS, Vernaison, France.

***eq*-Re$_2$(CO)$_9$(MeCN).** Following the literature procedure,[3]

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[22] Smith, C.; Boekelheide, V. In *Organic Syntheses*; Marvel, C. C., Ed.; Wiley: New York, 1973; Collect. Vol. V, p 872.

0.66 g (0.1 mmol) of $Re_2(CO)_{10}$ was dissolved in 50 mL of dichloromethane and 8 mL of MeCN. To this solution was added dropwise a solution of 0.15 g (0.2 mmol) of Me_3NO in 10 mL of dichloromethane, and the reaction was monitored by IR spectroscopy. The addition was stopped when the bands of $Re_2(CO)_{10}$ had completely disappeared. After removal of solvent, the crude product was chromatographed on silica gel plates with dichloromethane/pentane 1/1 as eluant. *eq*-$Re_2(CO)_9$(MeCN) was first isolated as a colorless solid (0.37 g, 56%), mp 113 °C (dichloromethane/pentane). IR (CH_2Cl_2): ν_{CO} at 2101 (w), 2044 (s), 1988 (vs), 1958 (s), 1927 cm^{-1} (s). ^1H NMR (CD_2Cl_2, 250 MHz): δ 2.41 (s, Me). ^{13}C NMR (CD_2Cl_2, 62.9 MHz): δ 200.45 (CO), 196.03 (br, CO), 193.35 (CO), 185.75 (CO), 126.44 (CN), 3.95 (Me). These agree with the literature data.[3] A second compound was isolated in low yield and identified as *dieq*-$Re_2(CO)_8(MeCN)_2$ (0.025 g, 4% yield), mp 162 °C dec. IR (CH_2Cl_2): ν_{CO} at 2069 (w), 2015 (s), 1965 (vs), 1904 cm^{-1} (s). ^1H NMR (CD_3COCD_3, 250 MHz): δ 2.65 ppm (s, Me). ^{13}C NMR (CD_3COCD_3, 62.9 MHz): δ 208.43 (4 CO), 197.59 (2 CO), 189.98 (2 CO), 128.67 (CN), 3.40 (Me). These are in accord with the literature data.[3]

***dieq*-$Re_2(CO)_8(MeCN)_2$.** A solution of Me_3NO (0.15 g, 2 mmol) in 10 mL of dichloromethane was added dropwise to a solution of $Re_2(CO)_{10}$ (0.66 g, 1 mmol) in 50 mL of dichloromethane and 8 mL of MeCN. After stirring at room temperature for 3 h, the solvent was removed and the product was purified by chromatography on silica gel plates with dichloromethane/pentane 1/1 as eluant. $Re_2(CO)_8(MeCN)_2$ was isolated as a yellow solid (0.37 g, 55% yield), mp 162 °C dec. $Re_2(CO)_9$(MeCN) was also isolated in 6% yield.

Reaction of *eq*-$Re_2(CO)_9$(MeCN) with Phenylacetylene and with 17α-Ethynylestradiol. *eq*-$Re_2(CO)_9$(MeCN) and phenylacetylene were heated under reflux in dichloromethane for 2 days. After this time the IR spectrum still showed $Re_2(CO)_9$(MeCN) to be the major component. TLC revealed the presence of several compounds, but none of them is present in sufficient quantity to allow isolation and characterization except for *eq*-$Re_2(CO)_9$(MeCN) which is recovered in 26% yield. A similar result was obtained in the reaction with α-ethynylestradiol.

(μ-H)(μ-C≡CPh)$Re_2(CO)_7$(MeCN) (1). *eq*-$Re_2(CO)_8(MeCN)_2$ (0.136 g, 0.2 mmol) and phenylacetylene (0.060 g, 0.5 mmol) were heated under reflux in 15 mL of dichloromethane for 5 h. The IR spectrum in the CO region showed only bands for (μ-H)(μ-C≡CPh)$Re_2(CO)_7$(MeCN). The solvent was removed under vacuum, and the crude product obtained was crystallized from CH_2Cl_2/pentane to yield colorless crystals (0.075 g, 54% yield), mp 156 °C. The IR and NMR data are summarized in Table I. EI MS (70 eV): m/z calcd for Re_2 = 372, 698 $[M]^+$, 670 $[M - MeCN]^+$, 642 $[M - MeCN - CO]^+$, 614 $[M - MeCN - 2CO]^+$, 586 $[M - MeCN - 3CO]^+$, 558 $[M - MeCN - 4CO]^+$, 532 $[M - MeCN - 5CO]^+$, 502 $[M - MeCN - 6CO]^+$, 474 $[M - MeCN - 7CO]^+$.

Synthesis of 17α-Ethynylestradiol Complex 2. $Re_2(CO)_8(MeCN)_2$ (0.339 g, 0.5 mmol) and α-ethynylestradiol (0.178 g, 0.6 mmol) were heated under reflux in 25 mL of dichloromethane for 15 h. The IR spectrum in the CO region showed only bands for the α-ethynylestradiol complex 2. The crude product obtained after solvent removal was chromatographed on silica gel plates by using diethyl ether/pentane/MeCN 10/5/1 as the eluant. Complex 2 (0.256 g, 58%), mp 150 °C dec, was extracted from silica gel as a colorless solid by using a mixture of diethyl ether/MeCN 5/1 as the solvent. Anal. Calcd for $C_{29}H_{27}O_9NRe_2$: C, 38.46; H, 3.00; N, 1.54. Found: C, 38.94; H, 3.44; N, 1.64.

Reactions of (μ-H)(μ-C≡CPh)$Re_2(CO)_7$(MeCN) (1). (a) With CO. A 0.050-g (0.07 mmol) amount of complex 1 was dissolved in 5 mL of toluene. The Schlenk tube was purged with CO gas at 1 atm and then the solution was heated at 70 °C for 2 h. The IR spectrum showed the formation of complex (μ-H)(μ-C≡CPh)$Re_2(CO)_8$ (3) which was isolated in quantative yield. Crystallization from pentane gave colorless crystals, mp 110 °C. The NMR and IR data were in agreement with those in the literature.[4a]

(b) With Pyridine. A 0.031-g (0.05 mmol) amount of complex 1 was dissolved in 5 mL of dichloromethane, 0.016 g (0.20 mmol) of pyridine was added, and the mixture was stirred for 1 h. The complex (μ-H)(μ-C≡CPh)$Re_2(CO)_7$(pyridine) (4) was formed in quantitative yield. Crystallization from dichloromethane/pentane gave light yellow crystals, mp 180 °C. The NMR and IR data were in agreement with the literature values.[4a] DCI MS: m/z 749 $[M]^+$, 721 $[M - CO]^+$.

(c) With PPh_3. A 0.107-g (0.15 mmol) amount of complex 1 and 0.040 g (0.15 mmol) of PPh_3 were dissolved in 1 mL of CD_2Cl_2. The ^1H NMR spectrum was measured within a few minutes and the reaction was already complete.

Reactions of 17α-Ethynylestradiol Complex 2. (a) With CO. A 0.091-g (0.10 mmol) amount of complex 2 was dissolved in 5 mL of benzene. The Schlenk tube was purged with CO gas at 1 atm, and the solution was heated at 75 °C for 15 h, after which time only the CO bands of 6 were visible in the IR spectrum. After removal of the benzene the crude product obtained was dissolved in dichloromethane. Complex 6 precipitated from the solution upon addition of hexane. A 0.060-g amount of complex 6 was collected as a colorless solid, but concentration of the solution and chromatography on silica gel plates (eluant:dichloromethane) yielded another 0.010 g of complex 6 (overall yield 52%), mp 130 °C dec. EI MS (70 eV): m/z 892 $[M]^+$, 874 $[M - H_2O]^+$, 846 $[M - H_2O - CO]^+$, 818 $[M - H_2O - 2CO]^+$, 790 $[M - H_2O - 3CO]^+$. Anal. Calcd for $C_{28}H_{24}O_{10}Re_2$: C, 37.68; H, 2.71. Found: C, 38.90; H, 3.28.

(b) With Pyridine. A 0.136-g (0.15 mmol) amount of complex 2 was dissolved in 15 mL of benzene. Two drops (0.016 g, 0.20 mmol) of pyridine were added, and the mixture was stirred for 1 h. The IR spectrum shows essentially CO bands of complex 7. Chromatography on silica gel plates using diethyl ether/pentane/MeCN 2/1/0.2 as the eluant, gives 0.080 g of a colorless solid of complex 7 (85% yield), mp 130 °C dec. EI MS (70 eV): m/z 846 $[M - py - H_2O]^+$, 818 $[M - py - H_2O - CO]^+$. Anal. Calcd for $C_{32}H_{29}O_9NRe_2$: C, 40.73; H, 3.10; N, 1.48. Found: C, 42.15; H, 3.69; N, 1.74.

(c) With PPh_3. A 0.072-g (0.08 mmol) amount of complex 2 and 0.021 g (0.08 mmol) of PPh_3 were dissolved in 0.5 mL of CD_2Cl_2. After 5 min the ^1H NMR spectrum showed that the substitution reaction was complete. The formation of complex 8 was confirmed by ^{13}C NMR and IR data. Crystallization from CD_2Cl_2/hexane gave a white solid, mp 168 °C dec. Anal. Calcd for $C_{45}H_{39}O_9PRe_2$: C, 47.96; H, 3.49. Found: C, 47.29; H, 3.85.

Reactivity of 17α-Ethynylestradiol Complex 6 with MeCN, Pyridine, and PPh_3. A 2-mg sample of complex 6 was dissolved in 0.4 mL of dichloromethane, and one drop of MeCN was added. The reaction was monitored by IR spectroscopy. The exchange was complete after 1 h, leading to the formation of complex 2.

In the same conditions, the reaction with pyridine and PPh_3 rapidly gave, within 10 min, respectively 7 and 8. These compounds were only identified by their IR values.

Reaction of 3 and 6 with *n*-$PrNH_2$. A 0.035-g (0.05 mmol) sample of complex 3 was dissolved in 3 mL of dichloromethane, and one drop of *n*-$PrNH_2$ (0.009 g, 0.1 mmol) was added. After stirring at room temperature for 2 h, the IR spectrum showed clean formation of a new complex in quantitative yield. After removal of solvent, the solid obtained was crystallized from CH_2Cl_2/hexane to yield colorless crystals of (μ-H)(μ-C≡CPh)-$Re_2(CO)_7$(n-Pr) (9), mp 140 °C. EI MS (70 eV): m/z calcd for Re_2 = 372 (M = 729), 670 $[M - (n\text{-}PrNH_2)]^+$, 416 $[M - (n\text{-}PrNH_2) - 2CO]^+$, 586 $[M - (n\text{-}PrNH_2) - 3CO]^+$, 558 $[M - (n\text{-}PrNH_2) - 4CO]^+$, 502 $[M - (n\text{-}PrNH_2) - 6CO]^+$, 474 $[M - (n\text{-}PrNH_2) - 7CO]^+$.

Under the same conditions, 6 (0.045 g, 0.05 mmol) reacts with *i*-$PrNH_2$, yielding the steroid complex (μ-H)(μ-C≡CR)$Re_2(CO)_7$(*i*-Pr) (9), mp 135 °C. The ^{13}C NMR and IR data are summarized in Table I. Anal. Calcd for $C_{30}H_{33}O_9NRe_2$: C, 39.00; H, 3.57; N, 1.52. Found: C, 40.29; H, 4.10; N, 2.00.

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Supplementary Material Available: A table of anisotropic temperature factors of 1 (1 page); a listing of structure factors for 1 (13 pages). Ordering information is given on any current masthead page.