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Synthesis, X-ray crystallographic, and reactivity studies of rhenium(V) alkyne complexes

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Abstract

$[ReOMe_2(bipy)(CH_3CN)][PF_6]$, prepared in situ, reacted with alkynes (ethyne, propyne, 2-butyne, 3-hexyne, phenylacetylene, and diphenylacetylene) to give the cationic alkyne complexes *trans*-$[ReOMe_2(bipy)(alkyne)][PF_6]$ (*trans*-Me–Re–Me). ^{1}H-NMR studies indicated that a *cis* isomer was formed initially. Kinetics studies showed that the isomerizations were first order in the alkyne complex. The observed rate constants depended on the steric bulk of the alkyne with bulkier alkynes producing smaller k_{obs} values. An Eyring plot for the isomerization of $[ReOMe_2(bipy)(2\text{-butyne})][PF_6]$ yielded $\Delta H^{\ddagger} = 21(1)$ kcal mol^{-1} and $\Delta S^{\ddagger} = 6(3)$ eu. The isomerization mechanism was proposed to involve the rearrangement of a five-coordinate intermediate formed by dissociation of a Re–N bond. Treatment of $[ReOMe_2(bipy)(CH_3CN)][PF_6]$ with dimethyl acetylenedicarboxylate afforded the metallacycle $[\overline{Re}\{C[C(O)OMe]C(Me)C(\overline{O})(OMe)\}(O)Me(bipy)][PF_6]$ via insertion of the alkyne into a Re–CH_3 bond. *Trans*-$[ReOMe_2(RCCH)(bipy)][PF_6]$ reacted with PMe_3 or PPh_3 to form the ylide complexes *cis*-$[ReOMe_2(bipy)\{C(R)CH(PR'_3)\}][PF_6]$ (R = H, R′ = Me or Ph; R = Ph, R′ = Me). In each case, a *trans* isomer (*trans*-Me–Re–Me) of the ylide complex was formed initially Spectroscopic and X-ray crystallographic studies suggest that the ylide complexes can be described as organometallic analogs of resonance-stabilized phosphonium ylides. The structures of *trans*-$[ReOMe_2(bipy)(PhCCPh)][PF_6]$, $[\overline{Re}\{C[C(O)OMe]C(Me)C(\overline{O})(OMe)\}(O)Me(bipy)][PF_6]$, *cis*-$[ReOMe_2(bipy)\{C(H)CH(PPh_3)\}][PF_6]$ and *cis*-$[ReOMe_2(bipy)\{C(Ph)CH(PMe_3)\}][PF_6]$ were determined by X-ray crystallography.

Keywords: Rhenium; Alkyne complexes; Ylide complexes; Alkyl complexes; Insertion reaction

1. Introduction

Nucleophilic attack at coordinated alkynes is a well-known reaction. Chisholm and Clark, for example, reported nucleophilic attack of RO^- on platinum–alkyne complexes [1], Bottrill and Green described similar reactions of hydride with molybdenum–alkyne complexes [2], and Reger carried out extensive studies on the addition of alkyls to cationic iron alkyne complexes [3]. More recently, it was reported that the addition of ethyne to $ReOR_3(PMe_3)$ formed $ReOR_3[C(H)CH(PMe_3)]$ via a mechanism proposed to involve ethyne displacement of PMe_3 and subsequent an attack on coordinated ethyne by external phosphine [4]. A similar mechanism was probably involved in the formation of $Re(Ndip)_2(CH_2CMe_3)[C(H)CH(PMe_2Ph)]$ from $Re(Ndip)_2(CH_2CMe_3)(PMe_2Ph)$(ethyne) reported by Schrock and co-workers. [5].

We described recently the synthesis of phosphine and acetonitrile adducts of cationic rhenium oxo-alkyl complexes [6]. As part of a broader study on the reactivity of these electrophilic compounds, we report here the syntheses of alkyne complexes and their subsequent reactions with phosphines to form ylide products by way of nucleophilic attack at the alkyne carbon.

2. Results and discussion

Scheme 1 summarizes our synthetic results.

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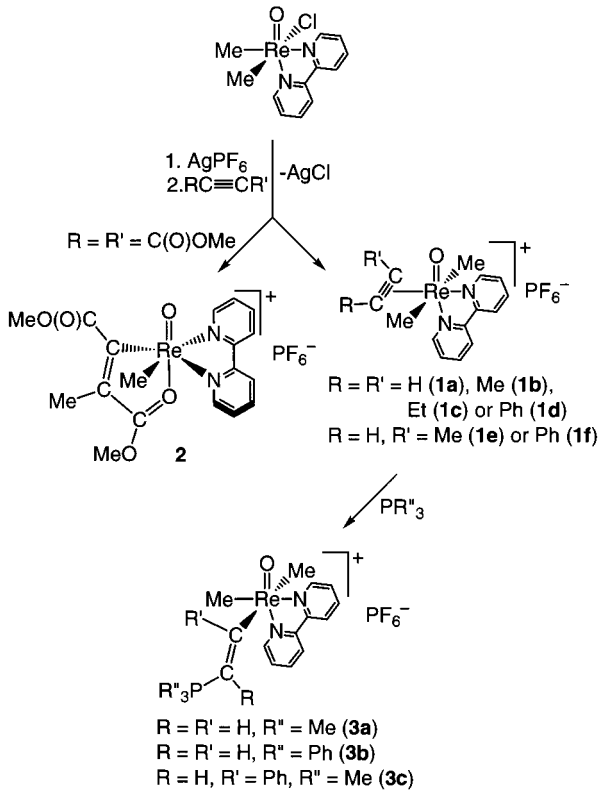


Scheme 1.

2.1. Synthesis of alkyne complexes

$[ReOMe_2(bipy)(CH_3CN)][PF_6]$, prepared in situ [6], reacts with excess alkyne in CH_2Cl_2–CH_3CN to give $[ReOMe_2(bipy)(alkyne)][PF_6]$ (alkyne = ethyne (**1a**), 2-butyne (**1b**), 3-hexyne (**1c**), diphenylacetylene (**1d**), propyne (**1e**) and phenylacetylene (**1f**); Scheme 1). The alkyne adducts are soluble in CH_2Cl_2 and CH_3CN, but not in hexanes, benzene, or diethyl ether. The moderately air-sensitive compounds are dark colored in powder form and give purple solutions (with the exception of **1d**, which gives dark brown solutions).

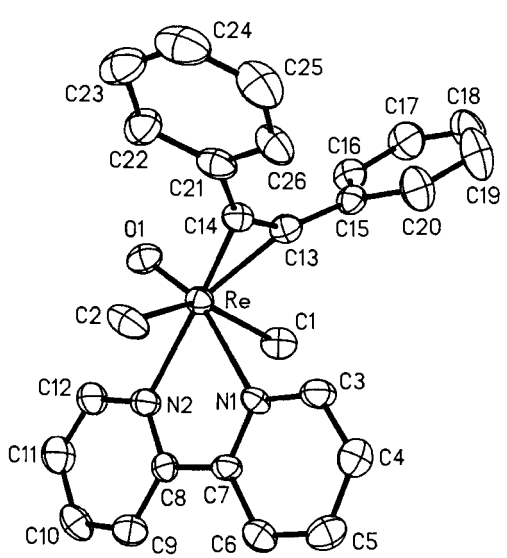


Fig. 1. Thermal ellipsoid plot of *trans*-$[ReOMe_2(bipy)(PhCCPh)][PF_6]$ (**1d**) showing the atom numbering scheme (40% probability ellipsoids).

An X-ray crystallographic study on **1d** was carried out to confirm the structural assignments. A thermal ellipsoid plot is shown in Fig. 1, crystallographic data are presented in Table 1, and selected bond distances and angles are given in Table 2. In the molecule, the alkyne C–C bond and the plane of the bipy lie, respectively, nearly perpendicular and parallel to the Re–O bond vector.

The Re–C(alkyne) distances (average 2.064(8) Å) are shorter than the Re–CH_3 bond distances (average 2.187(8) Å), and the alkyne C–C distance (1.313(11) Å) is close to the value for a C–C double bond (1.34 Å). For comparison, the Re–C(alkyne) and C–C distances in $ReOMe_3(PhCCPh)$ are 2.090(7) and 1.290(14) Å, respectively [4]. The alkyne substituents in **1d** are bent away from the metal center by about 37°, a typical value for alkyne complexes [7]. The Re–O and Re–CH_3 distances are within the range of distances reported previously [4,6,8]. The Re–N(1) distance (2.284(6) Å) is longer than the Re–N(2) distance (2.200(6) Å) due to the *trans* influence of the oxo group. The Re atom is displaced by 0.37 Å from the plane defined by C(13), C(14), C(1), C(2), and N(2) in the direction of the oxygen atom.

One singlet is observed in ^{1}H-NMR spectra for the methyl ligands in **1a**–**d**, as expected for *trans* methyl groups, and two singlets are observed for the methyl ligands in **1e**–**f**. In the latter case, the *cis* and *trans* geometries cannot be distinguished by ^{1}H-NMR spectroscopy, since both isomers would give rise to two different methyl ligand resonances. We assume that **1e**–**f** have *trans* geometries by analogy to **1a**–**d**. A ^{1}H-^{1}H COSY spectrum for **1e** shows that the propyne proton couples weakly ($^4J_{HH} = 1.5$ Hz) to the propyne methyl group. For all the molecules, the bipyridine protons give rise to eight resonances, as expected. The ethyne ^{13}C shift in **1a**, determined by recording the spectrum of $H^{13}C^{13}CH$ labeled **1a**, is 148 ppm (CD_3CN). The *cis* isomer of **1a** (*cis*-Me–Re–Me), which is the kinetic product of the reaction between the cation and ethyne (see below), has an ethyne carbon shift of 121 ppm. The reason for the 27 ppm difference in chemical shifts between the *cis* and *trans* isomers is unclear but might reflect a stronger *trans* influence from the methyl ligand *trans* to the alkyne ligand in the *cis* isomer compared to having a nitrogen of the bipy ligand *trans* to the alkyne in the *trans* isomer. The chemical shifts of 121 and 148 ppm classify the alkyne ligands as two- and three-electron donors, respectively, according to Templeton's NMR criterion [9]. The 121

Table 1

Crystallographic data for $[ReOMe_2(bipy)(PhCCPh)][PF_6]$ (**1d**), $[Re\{C[C(O)OMe]C(Me)C(O)(OMe)\}(O)Me(bipy)][PF_6]$ (**2**), $[ReOMe_2(bipy)\{C(H)CH(PPh_3)\}][PF_6]\cdot C_7H_8$ (**3b**·C_7H_8) and $[ReOMe_2(bipy)\{C(Ph)CH(PMe_3)\}][PF_6]\cdot C_7H_8$ (**3c**·C_7H_8)

Compound	**1d**	**2**	**3b**·C_7H_8	**3c**·C_7H_8
Formula	$C_{26}H_{24}N_2ORePF_6$	$C_{18}H_{20}N_2O_5RePF_6$	$C_{32}H_{31}N_2OPRePF_6\cdot C_7H_8$	$C_{23}H_{29}N_2OPRePF_6\cdot C_7H_8$
Formula weight	711.69	675.53	913.86	803.76
Crystal dimensions (mm)	$0.08\times0.25\times0.60$	$0.38\times0.22\times0.20$	$0.40\times0.15\times0.10$	$0.20\times0.18\times0.06$
Space group	$P2_1/n$ (monoclinic)	$P\bar{1}$ (triclinic)	$I2/c$ (monoclinic)	$P\bar{1}$ (triclinic)
a (Å)	16.500(4)	9.5090(7)	34.918(2)	10.3210(6)
b (Å)	12.347(2)	10.2418(7)	10.9309(7)	10.5599(6)
c (Å)	13.083(4)	12.5591(9)	20.4565(13)	15.7105(10)
α (°)		75.8480(10)		95.2930(10)
β (°)	99.14(2)	69.0220(10)	97.9360(10)	93.5210(10)
γ (°)		84.1300(10)		102.9060(10)
Temperature (°C)	−50	−50	−50	−50
Z	4	2	8	2
V (Å^3)	2632	1107.24(14)	7733.1(8)	1656.0(2)
$D_{calc.}$ (g cm^{-3})	1.80	2.026	1.570	1.612
μ (cm^{-1})	48.0	56.43	32.87	38.25
R, R_w [a]	0.029, 0.029 [b]	0.0208, 0.0546 [c]	0.0244, 0.0555 [d]	0.0282, 0.0705 [e]

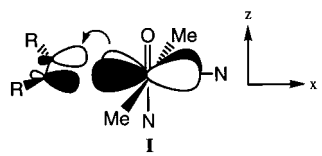
[a] $R=\Sigma\big||F_o|-|F_c|\big|/\Sigma|F_o|$, $R_w=[\Sigma\, w(F_o^2-F_c^2)^2/\Sigma\, w(F_o^2)^2]^{1/2}$.
[b] $w=[\sigma(F)]^{-2}$.
[c] $w=[\sigma^2(F_o^2)+(0.0232P)^2+(1.9990P)]^{-1}$ where $P=(F_o^2+2F_c^2)/3$.
[d] $w=[\sigma^2(F_o^2)+(0.0194P)^2+(24.5578P)]^{-1}$ where $P=(F_o^2+2F_c^2)/3$.
[e] $w=[\sigma^2(F_o^2)+(0.0366P)^2+(3.7580P)]^{-1}$ where $P=(F_o^2+2F_c^2)/3$.

Table 2
Bond distances (Å) and angles (°) for $[ReOMe_2(bipy)(PhCCPh)][PF_6]$ (**1d**)

Bond distances					
Re–O(1)	1.669(5)	Re–N(1)	2.284(6)	Re–N(2)	2.200(6)
Re–C(1)	2.185(7)	Re–C(2)	2.188(8)	Re–C(13)	2.062(8)
Re–C(14)	2.065(8)	C(13)–C(14)	1.313(11)		
Bond angles					
O(1)–Re–N(1)	158.6(3)	O(1)–Re–N(2)	87.5(3)	O(1)–Re–C(1)	102.1(3)
O(1)–Re–C(2)	104.0(3)	O(1)–Re–C(13)	105.6(3)	O(1)–Re–C(1)	104.9(3)
N(1)–Re–N(2)	71.1(2)	N(1)–Re–C(1)	74.2(3)	N(1)–Re–C(2)	73.7(3)
N(1)–Re–C(13)	94.5(3)	N(1)–Re–C(14)	95.6(3)	N(2)–Re–C(1)	80.7(3)
N(2)–Re–C(2)	79.4(3)	N(2)–Re–C(13)	157.9(3)	N(2)–Re–C(14)	156.4(3)
C(1)–Re–C(2)	146.2(3)	C(1)–Re–C(13)	79.2(3)	C(1)–Re–C(14)	115.2(3)
C(2)–Re–C(13)	113.4(3)	C(2)–Re–C(14)	78.1(3)	C(13)–Re–C(14)	37.1(3)
C(13)–C(14)–C(21)	144.1(8)	C(14)–C(13)–C(15)	141.7(8)		

ppm value is at the high end of the two-electron donor range (95–125 ppm; the three-electron donor range is ≈140–190 ppm) [9]. Three-electron donation was attributed to the alkynes in $ReOMe_3$(alkyne) complexes based on similar NMR data (139–148 ppm) [4]. In the latter case, the three-electron alkyne donation was rationalized by a group theoretical analysis, which also indicated that the oxo group donates five electrons to the metal center. By applying the same group theoretical analysis, it appears that **1a–f** are 18-electron compounds, with the oxo, alkyne, methyl, and bipy ligands contributing five, three, four, and four electrons, respectively.

The alkynes in the $[ReOMe_2(bipy)(alkyne)]^+$ complexes are perpendicular to the Re–O bond vector because π bonding between the alkyne π* and rhenium-based HOMO is maximized in this geometry, as illustrated in **I** [4].

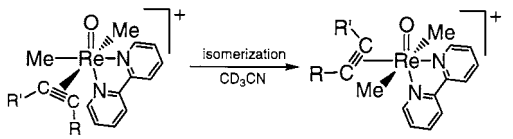


I

2.2. Cis–trans isomerization of $[ReOMe_2(bipy)(alkyne)]^+$

To understand better the formation of the alkyne complexes, several reactions were carried out in NMR tubes and monitored by ^{1}H-NMR spectroscopy. It was

found that *cis*-$ReOMe_2(bipy)Cl$, $AgPF_6$, and alkyne react in acetonitrile-d_3 solvent to form initially *cis*-$[ReOMe_2(bipy)(alkyne)][PF_6]$, which isomerizes to the *trans* isomer (Eq. (1)).



(1)

Kinetics studies on selected alkyne derivatives indicate that the *cis–trans* isomerization is first order in the alkyne complex. At room temperature (r.t.), the rate constants, determined by monitoring the disappearance of the *cis* isomer, depend on the steric bulk of the alkyne substituents, with larger substituents giving smaller rate constants: $k_{obs}(21.5°C) = 3.07$ (2-butyne), 2.43 (3-hexyne), 0.672 (phenylacetylene), and 0.218 (diphenylacetylene) $\times 10^{-4}$ s^{-1}. An Eyring plot (5.0, 20.0, 21.5, 25.0, and 30.0(0.1)°C) for the isomerization of **1b** yields $\Delta H^{\ddagger} = 21(1)$ kcal mol^{-1} and $\Delta S^{\ddagger} = 6(3)$ eu (Fig. 2).

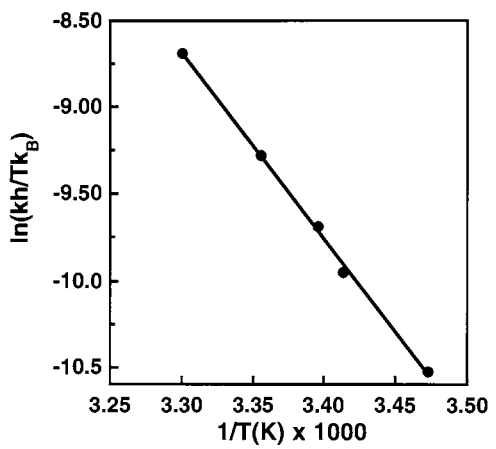
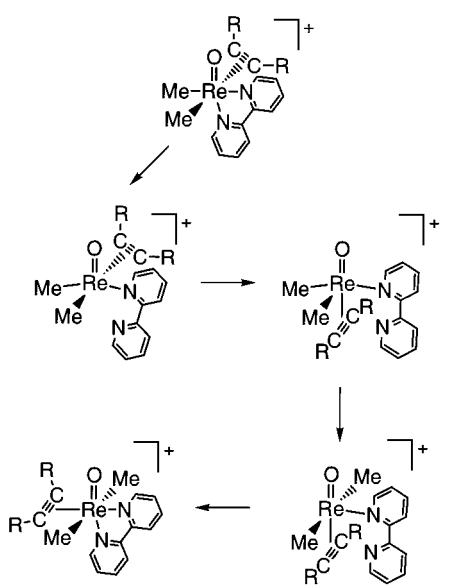


Fig. 2. Eyring plot of the isomerization of *cis*-$[ReOMe_2(bipy)(MeCCMe)][PF_6]$ to *trans*-$[ReOMe_2(bipy)(MeCCMe)][PF_6]$ (**1b**), where k is the rate constant, h is Planck's constant, k_B is Boltzmann's constant, and T is the temperature in Kelvin.



Scheme 2.

To further probe the isomerization mechanism, the *cis–trans* isomerization of **1f** was monitored at r.t. in the presence of approximately two and ten equivalents of phenylacetylene. The rate constants for the two different reactions determined by monitoring the disappearance of the *cis* isomer differ by 6%, and those based on the appearance of the *trans* isomer differ by 18%, which is probably still within experimental error. The rate constant (based on the disappearance of *cis* isomer) is independent of whether PF_6^- or $CF_3SO_3^-$ is the counterion (the difference in k_{obs} is about 5%). These studies suggest that neither the counterion nor dissociation of alkyne is involved in the *cis–trans* isomerization.

The room-temperature isomerization of **1f** in the presence of approximately ten equivalents of bipy or 100 equivalents of pyridine-d_5 was also examined. In the presence of excess bipy, the rate constant based on the disappearance of the *cis* isomer is within experimental error of the value in the absence of added bipy. In the presence of excess pyridine-d_5, the rate constant based on the disappearance of the *cis* isomer is about 20% larger than when no excess pyridine is added. A much larger difference in rate constants, however, is observed upon comparing the rate constants determined from the *appearance* of the *trans* isomer versus the *disappearance* of the *cis* isomer. When no bipy or pyridine is added, the rate constants vary by only 2%, but, in the presence of excess bipy or pyridine, the rate constants determined from the appearance of the *trans* isomer are, respectively, 37 and 144% smaller than the rate constants based on the disappearance of the *cis* isomer. A pathway involving the disruption of one Re–N bond is a possible rationalization for this result — the excess bipyridine and pyridine could compete for the empty coordination site left by the dissociation at one end of the bipy ligand. An intermediate with a second bipy or pyridine coordinated, however, was not observed directly. Given these considerations and the small entropy of activation found for the isomerization of **1b**, the stepwise route shown in Scheme 2, in which the weak Re–N bond *trans* to the oxo ligand dissociates to give a five-coordinate intermediate, represents a plausible mechanism for the *cis–trans* isomerization. Similar pathways involving five-coordinate intermediates in which a methyl ligand moves *trans* to the oxo group or one in which the Re–N bond *cis* to the oxo group dissociates initially are also possibilities. A least-motion pathway through a tbp structure in which both nitrogens remain attached to Re and the midpoint between

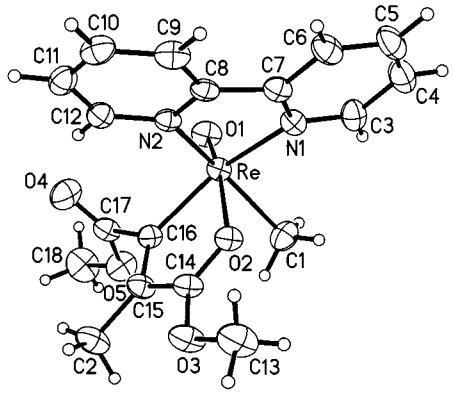


Fig. 3. Thermal ellipsoid plot of [Re{C[C(O)OMe]C(Me)C(O)(OMe)}(O)Me(bipy)][PF_6] (**2**) showing the atom numbering scheme (40% probability ellipsoids).

the nitrogens defines an apical position *trans* to the oxo ligand cannot be excluded, but such a mechanism is inconsistent with the results of the kinetics runs in the presence of excess bipy and pyridine-d_5.

2.3. Formation of a metallacycle

[$ReOMe_2$(bipy)(CH_3CN)][PF_6], prepared in situ, reacts with dimethyl acetylenedicarboxylate in acetonitrile to give the oxametallacyclic compound, [Re{C[C(O)OMe]C(Me)C(O)(OMe)}(O)Me(bipy)][PF_6] (**2**) via the insertion of the alkyne into a Re–Me bond (see Scheme 1). The proton NMR data are consistent with initial formation of *cis*-[$ReOMe_2$(bipy)-{MeO(O)CC≡CC(O)OMe}]$^+$ and subsequent conversion to the *trans* isomer, which appears to be the immediate precursor to the metallacycle.

An X-ray crystallographic study of **2** was performed. A thermal ellipsoid plot of the molecule is shown in Fig. 3, crystallographic data are given in Table 1, and selected bond distances and angles are presented in Table 3.

The Re=O (1.667(3) Å) and Re–C(1) (2.114(5) Å) bond distances in **2** are within the range of distances reported previously [4,6,8]. The Re–C(16) distance (2.062(4) Å) is about 0.05 Å shorter than the Re–CH_3 distance, but it is significantly longer than the Re=C bonds in ReO_2[=C(H)-*t*-Bu](CH_2-*t*-Bu) (1.869(9) Å) [10] and other related high-oxidation-state rhenium alkylidene complexes [11]. A more relevant comparison is probably to the Re–C_{sp^2} bond distance in the alkenyl cluster $Re_3(\mu\text{-O-}i\text{-Pr})_3(O\text{-}i\text{-Pr})_5(\eta^1\text{-CPh=CH}_2)$ (2.124(17) Å) [12]. The C(15)–C(16) (1.342(6) Å) and C(14)–C(15) (1.455(6) Å) bond distances are typical double and C_{sp^2}–C_{sp^2} single C–C bond distances, respectively, but C(14)–C(15) within the metallacycle is slightly shorter than C(16)–C(17) (1.505(6) Å), which is *exo* to the ring. The O(2)–C(14) bond (1.244(5) Å) is lengthened slightly compared with O(4)–C(17) (1.192(6) Å) because of the Re–O(2) interaction. The Re–O(2) distance (2.264(3) Å) is long compared with the terminal (1.90–1.93 Å) and bridge (2.08–2.12 Å) bonded Re–OR distances in $Re_3(\mu\text{-OCH}_2\text{CMe}_3)_3(OCH_2CMe_3)_6$ [13], which is consistent with Re–O(2) being a dative O→Re interaction. The metallacyclic ring is nearly planar, with a r.m.s. deviation of 0.014 Å.

The ^{1}H-NMR spectrum for **2** is consistent with the solid-state structure by having four different singlets arising from the methyl groups and eight peaks from the bipyridine ligand. In the ^{13}C-NMR spectrum, the ring C_α chemical shift is 197 ppm. This value is downfield of the C_α resonance of 153 ppm for $Re_3(\mu\text{-O-}i\text{-Pr})_3(\eta^1\text{-C(H)=C(H)Ph})(O\text{-}i\text{-Pr})_5$ [12], but not in the range typically found for Schrock-type rhenium alkylidene complexes such as ReO_2[=CH-*t*-Bu](CH_2-*t*-Bu) (δ(Re=*C*) 283 ppm) [10], Re(≡C-*t*-Bu)(=CH-*t*-Bu)(O-*t*-Bu)$_2$ (231 ppm) [11a] and [Re(≡C-*t*-Bu)(=CH-*t*-Bu)(CH_2-*t*-Bu)(CH_3CN)$_2$][BF_4] (292 ppm) [14].

Table 3
Bond distances (Å) and angles (°) for [Re{C[C(O)OMe]C(Me)C(O)(OMe)}(O)Me(bipy)][PF_6] (**2**)

Bond distances					
Re–O(1)	1.667(3)	O(2)–C(14)	1.244(5)	C(2)–C(15)	1.507(6)
Re–C(16)	2.062(4)	O(3)–C(14)	1.317(5)	C(14)–C(15)	1.455(6)
Re–C(1)	2.114(5)	O(3)–C(13)	1.456(6)	C(15)–C(16)	1.342(6)
Re–N(1)	2.124(3)	O(4)–C(17)	1.192(6)	C(16)–C(17)	1.505(6)
Re–N(2)	2.133(3)	O(5)–C(17)	1.327(6)	O(5)–C(18)	1.455(6)
Re–O(2)	2.264(3)				
Bond angles					
O(1)–Re–C(1)	100.10(20)	N(1)–Re–N(2)	75.09(13)	C(14)–O(2)–Re	113.5(2)
O(1)–Re–N(1)	111.76(14)	C(16)–Re–C(1)	89.3(2)	O(2)–C(14)–C(15)	120.4(4)
O(1)–Re–N(2)	110.48(14)	C(16)–Re–N(1)	150.4(2)	C(16)–C(15)–C(14)	111.2(4)
O(1)–Re–C(16)	97.70(20)	C(16)–Re–N(2)	91.9(2)	C(15)–C(16)–Re	122.0(3)
O(1)–Re–O(2)	169.75(13)	C(1)–Re–N(1)	88.8(2)	C(17)–C(16)–Re	119.5(3)
C(16)–Re–O(2)	72.91(13)	C(1)–Re–O(2)	76.3(2)	C(16)–C(15)–C(2)	127.9(4)

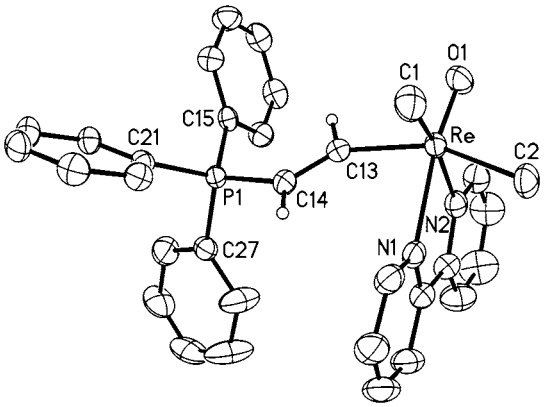


Fig. 4. Thermal ellipsoid plot of *cis*-[ReOMe$_2$(bipy){C(H)CH-(PPh$_3$)}][PF$_6$] (**3b**) showing the atom numbering scheme (40% probability ellipsoids).

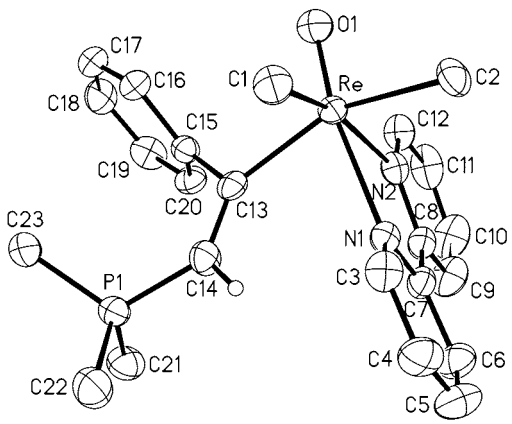
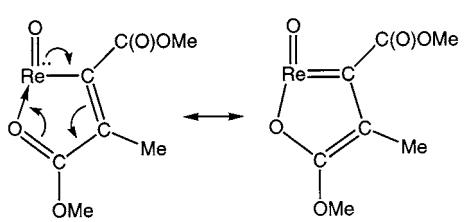


Fig. 5. Thermal ellipsoid plot of *cis*-[ReOMe$_2$(bipy){C(Ph)CH-(PMe$_3$)}][PF$_6$] (**3c**) showing the atom numbering scheme (40% probability ellipsoids).

Taken together, the structural and spectroscopic data suggest **IIa** is the appropriate resonance form to describe **2**, with perhaps some contribution from **IIb**.



2.4. Addition of PR_3 to coordinated alkyne

Reactions of trimethylphosphine with **1a** and **1f**, and triphenylphosphine with **1a** form the ylide complexes *cis*-[ReOMe$_2$(bipy){C(R′)CR(PR$'_3$)}][PF$_6$] (R = R′ = H, R′ = Me (**3a**) or Ph (**3b**); R = H, R′ = Ph, R″ = Me (**3c**); Scheme 1). The compounds are obtained as dark red crystalline solids that are soluble in CH_2Cl_2 and CH_3CN, sparingly soluble in toluene and diethyl ether, and insoluble in hexanes. The reactions to form the ylides were monitored by ^{1}H-NMR spectroscopy. The spectra indicate that in each case a *trans* isomer (*trans*-Me–Re–Me) of the ylide complex forms initially, which isomerizes to the *cis* isomer. Presumably, the *trans* → *cis* isomerization mechanism is similar to the *cis* → *trans* isomerization proposed for the parent alkyne complexes (Scheme 2). The reason why the ylide complexes **3** prefer the *cis* geometry and the alkyne complexes (**1a**–**f**) prefer the *trans* form in the respective thermodynamic products is not clear to us.

While monitoring the formation of **3c** by ^{1}H-NMR spectroscopy, a small amount (1–2%) of the isomer derived from the phosphine attack on Ph*C*≡CH was observed (δ 10.8, J_{PH} = 38 Hz, ReC*H*CPh(PMe$_3$)). The reason for the large predominance of the Re–C(Ph)-CH(PMe$_3$) product over the Re–C(H)CPh(PMe$_3$) isomer is probably a consequence of steric control.

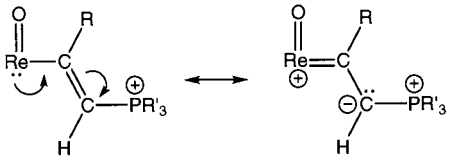
X-ray crystallographic studies of **3b** and **3c** were performed. Thermal ellipsoid plots are shown in Figs. 4 and 5, crystallographic data are given in Table 1, and selected bond distances and angles are presented in Table 4.

The Re–O and Re–CH_3 bond distances are within the range of distances found previously [4,6,8]. The Re–C(13) distances (av. 2.06 Å) are shorter than typical Re–C(alkyl) bond lengths and are close to the Re–C(16) distance (2.062(4) Å) in the metallacycle **2**. The C(13)–C(14) distances (av. 1.34 Å) are typical C–C double bond distances, while the P–C(14) distances (av. 1.76 Å) are similar to the P–CH_3 (av. 1.786(6) Å) and P–C_6H_5 (av. 1.800(4)) distances. The P–C(14) distances are longer than the P–C_{ylide} distance in Ph_3PCH_2 (1.661(8) Å) [15], but they are comparable to those in the resonance-stabilized ylides triphenylphosphonium cyclopentadienylide (1.718(2) Å) [16] and triphenylphosphonium dicyanomethylide (1.753(8) Å) [17].

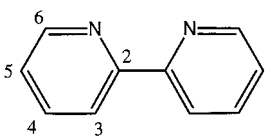
The spectroscopic data for **3** are informative. The chemical shifts of the ylide carbon resonances (98–105 ppm) are close to the value reported for C_{ylide} in resonance-stabilized triphenylphosphonium cyclopentadienylide (78 ppm) [18], and are far downfield of the shifts reported for ylides such as Me_3PCH_2 (−2.4 ppm) [18a]. The ^{13}C chemical shifts for C_α (Re–*C*) of the ReCR′ = CR(PR$''_3$) groups are in the range 192–217 ppm, which are between the C_α shift in $Re_3(\mu\text{-O-}i\text{-Pr})_3(\eta^1\text{-C(H)=C(H)Ph)(O-}i\text{-Pr)}_5$ [12], and the range found for Schrock-type rhenium alkylidenes [11,14] (see discussion in the previous section concerning **2**). The spectroscopic and structural data for **3** are in accordance with data reported for related ylide complexes such as $(OC)_5M[C(OSiMe_3)CH(PMe_3)]$ (M = Cr, Mo, W) [19], $ReO(CH_2SiMe_3)_3[C(H)CH(PMe_3)]$, and $[Re(O)Me_2\{C(H)CH(PMe_2Ph)\}_2]^+$ [4].

The spectroscopic and structural data for **3** suggest that the bonding can be described as a resonance

composite of **IIIa** and **IIIb** (i.e. **3a**–**c** are organometallic analogs of a resonance-stabilized phosphonium propenylide) with **IIIa** being the dominant contributor. A similar conclusion was reached for ReO-$(CH_2SiMe_3)_3$[C(H)CH(PMe_3)] and [Re(O)Me_2{C(H)-CH(PMe_2Ph)}$_2$]$^+$ [4].



III



IV

3. Conclusions

Cis-ReOMe$_2$(bipy)Cl reacted with $AgPF_6$ and RCCR′ (R = R′ = H, Me, Et or Ph; R = H, R′ = Me or Ph) to give [ReOMe$_2$(bipy)(RCCR′)][PF_6] compounds and with $AgPF_6$ and dimethyl acetylenedicarboxylate to give the metallacycle [Re{C[C(O)OMe]C(Me)C(O)-(OMe)}(O)Me(bipy)][PF_6], a product of acetylene insertion into a Re–Me bond. In all of the reactions, the *cis*-Me–Re–Me isomer of [ReOMe$_2$(bipy)(RCCR′)]-[PF_6] formed initially and then converted to the thermodynamically more stable *trans* geometry. In the reaction involving dimethyl acetylenedicarboxylate, the *trans* isomer appeared to be the immediate precursor to the metallacyclic compound. Based on kinetics and related NMR studies, we propose that the *cis*–*trans* isomerization mechanism involves dissociation of one Re–N bond followed by rearrangement of the five-coordinate intermediate.

Phosphines reacted with *trans*-[ReOMe$_2$(bipy)-(RCCR′)][PF_6] to form the ylide complexes *cis*-[ReOMe$_2$(bipy){C(R)CH(PR'_3)}][PF_6] (R = H, R′ = Me or Ph; R = Ph, R′ = Me). In each case, a *trans* isomer (*trans*-Me–Re–Me) of the ylide complex formed initially. Spectroscopic and X-ray crystallographic studies suggest that the ylide compounds can be described as organometallic analogs of resonance-stabilized phosphonium ylides.

Table 4
Bond distances (Å) and angles (°) for [ReOMe$_2$(bipy){C(H)CH(PPh_3)}][PF_6] (**3b**) and [ReOMe$_2$(bipy){C(Ph)CH(PMe_3)}][PF_6] (**3c**)

	3b	**3c**
Bond distances		
Re–O(1)	1.687(3)	1.689(4)
Re–C(1)	2.132(4)	2.137(5)
Re–C(2)	2.142(4)	2.158(5)
Re–N(1)	2.287(3)	2.296(4)
Re–N(2)	2.204(3)	2.151(4)
Re–C(13)	2.033(4)	2.087(5)
C(13)–C(14)	1.340(5)	1.338(7)
P(1)–C(14)	1.754(4)	1.774(5)
C(13)–C(15)		1.507(7)
Bond angles		
O(1)–Re–C(1)	103.4(2)	104.6(2)
O(1)–Re–C(2)	105.1(2)	101.5(2)
O(1)–Re–C(13)	105.0(2)	106.2(2)
O(1)–Re–N(2)	89.8(1)	94.8(2)
O(1)–Re–N(1)	160.1(1)	165.1(2)
N(1)–Re–N(2)	70.4(1)	71.11(14)
C(1)–Re–C(13)	85.7(2)	83.9(2)
C(2)–Re–C(13)	149.6(2)	152.0(2)
N(2)–Re–C(13)	93.2(1)	91.1(2)
N(1)–Re–C(13)	78.3(1)	79.7(2)
C(1)–Re–C(2)	83.4(2)	85.1(2)
Re–C(13)–C(14)	141.0(3)	133.5(4)
P(1)–C(14)–C(13)	122.9(3)	130.3(4)
Re–C(13)–R	105(2) [R = H(13)]	110.1(3) [R = C(15)]
C(13)–C(14)–H(14)	123(3)	120(4)
C(14)–C(13)–R	114(2) [R = H(13)]	116.5(5) [R = C(15)]
P(1)–C(14)–H(14)	113(3)	110(4)

4. Experimental

Unless otherwise stated, all reactions were performed in flame-dried or oven-dried glassware using standard Schlenk and glovebox techniques. Solvents were purified by standard techniques. Rhenium metal was purchased from Cleveland Refractory Materials and used as received. $ReOMe_2(bipy)Cl$ was prepared as described in the literature [6]. Nuclear magnetic resonance spectra were recorded on a 300 MHz instrument. Phosphorus NMR spectra were referenced to external H_3PO_4 with positive chemical shifts downfield.

4.1. *trans*-[$ReOMe_2(bipy)(HCCH)][PF_6]$ (**1a**)

$ReOMe_2(bipy)Cl$ (0.10 g, 0.24 mmol) was dissolved in CH_2Cl_2–CH_3CN (15–2 ml) and $AgPF_6$ (0.060 g, 0.24 mmol) was added to the solution. The red–purple solution changed immediately to green, and a white precipitate appeared, indicating [$ReOMe_2(bipy)$-(NCMe)][PF_6] had been generated. The mixture was stirred for 1 h and then filtered. The green filtrate was frozen in liquid nitrogen, and ethyne (≈ 1.0 mmol) was added to the flask via a calibrated vacuum manifold. The solution was allowed to warm to r.t., whereupon the color changed to light red. The mixture was stirred for 3 h. The solvent was removed in vacuo, and the dark blue residue was extracted with CH_2Cl_2 (2×25 ml). The extracts were filtered, and the combined filtrates were then reduced in volume to approximately 10 ml. The solution was layered with hexane (30 ml). The product crystallized at r.t. as the layers mixed. There was a dark blue film on the bottom of the flask after the mother liquor was removed. Under the microscope, the isolated material was composed of very thin blue needles that had blue–green material attached to them. The compound was pure by NMR spectroscopy and chemical analysis (yield 0.052 g, 70%). Anal. Calc. for $C_{14}H_{16}N_2ORePF_6$: C, 30.06; H, 2.88; N, 5.01. Found. C, 29.97; H, 2.87; N, 4.73%.

^{1}H-NMR (CD_2Cl_2): δ 10.46 (s, 2, *HCCH*), 9.41 (d, 1, $J_{HH} = 4.8$ Hz, bipy), 8.73 (d, 1, $J_{HH} = 8.1$ Hz, bipy), 8.55 (dt, 1, $J_{HH} = 8.1$, $J_{HH} = 1.2$ Hz, bipy), 8.44 (d, 1, $J_{HH} = 8.1$ Hz, bipy), 8.09 (dt, 1, $J_{HH} = 8.1$, $J_{HH} = 1.2$ Hz, bipy), 7.91 (dt, 1, $J_{HH} = 7.2$, $J_{HH} = 0.9$ Hz, bipy), 7.37 (dt, 1, $J_{HH} = 6.6$, $J_{HH} = 0.9$ Hz, bipy), 7.10 (d, 1, $J_{HH} = 5.4$ Hz, bipy), 2.24 (s, 6, Re*Me*$_2$). ^{13}C{^{1}H} (CD_2Cl_2): δ 153, 152, 151, 148, 147, 143, 141, 130, 129, 127, 125, 24.3 (Re*Me*$_2$). ^{13}C{^{1}H} (CD_3CN): δ 148 (H^{13}*C*^{13}*C*H). IR (KBr, Nujol, cm^{-1}) 1659 w, 1607 s, 1402 w, 1319 w, 1165 m, 1076 w, 1024 w, 983 s, 902 m, 839 s, 767 m, 723 m, 678 w, 667 w.

4.2. *trans*-[$ReOMe_2(bipy)(MeCCMe)][PF_6]$ (**1b**)

This compound was prepared by a procedure analogous to the one used to prepare **1a**. The compound was isolated as golden yellow crystals (yield 40%). Anal. Calc. for $C_{16}H_{20}N_2ORePF_6$: C, 32.71; H, 3.43; N, 4.77. Found. C, 32.50; H, 3.25; N, 5.01%.

^{1}H-NMR (CD_2Cl_2): δ 9.44 (d, 1, $J_{HH} = 6.3$ Hz bipy), 8.67 (d, 1, $J_{HH} = 8.1$ Hz, bipy), 8.52 (dt, 1, $J_{HH} = 8.1$, $J_{HH} = 1.5$ Hz, bipy), 8.42 (d, 1, $J_{HH} = 8.1$ Hz, bipy), 8.04 (dt, 1, $J_{HH} = 8.1$, $J_{HH} = 1.5$ Hz, bipy), 8.00 (t, 1, $J_{HH} = 6.6$ Hz, bipy), 7.40 (t, 1, $J_{HH} = 6.6$ Hz, bipy), 6.95 (d, 1, $J_{HH} = 5.4$ Hz, bipy), 3.24 (s, 6, *Me*CC*Me*), 1.91 (s, 6, Re*Me*$_2$). ^{13}C{^{1}H}-NMR (CD_2Cl_2): δ 156, 152, 151, 149, 147, 143, 141, 129, 128, 126, 125, 25.6 (Re*Me*$_2$), 12.5 (*Me*CC*Me*). IR (KBr, Nujol, cm^{-1}): 1606 s 1753 br, 1417 w, 1303 w, 1155 m, 1020 m, 970 s, 839 s, 723 sh, 603 sh, 566 m.

4.3. *trans*-[$ReOMe_2(bipy)(EtCCEt)][PF_6]$ (**1c**)

To a green solution of [$ReOMe_2(bipy)(CH_3CN)$]-[PF_6], prepared in situ from $ReOMe_2(bipy)Cl$ (0.086 g, 0.20 mmol) and $AgPF_6$ (0.050 mg, 0.20 mmol) in CH_2Cl_2–CH_3CN (15–0.5 ml), was added 3-hexyne (25 μl, 0.22 mmol) via microsyringe. The red mixture was stirred for 1 h. The mixture was filtered, and the filtrate was taken to dryness in vacuo. The residue was washed with benzene (2×5 ml) and diethyl ether (2×5 ml). The residual dark powder was dissolved in CH_2Cl_2 (5 ml), and then layered with hexanes (15 ml). After 1 day at r.t., a dark powder formed (yield 0.078 g, 65%). Anal. Calc. for $C_{18}H_{24}N_2ORePF_6$: C, 35.12; H, 3.93; N, 4.55. Found: C, 35.10; H, 3.60; N, 4.58%.

^{1}H-NMR (CD_3CN): see **IV** for numbering system. δ 9.40 (ddd, 1, $^3J_{65} = 5.7$, $^4J_{64} = 1.5$, $^5J_{63} = 0.8$ Hz, bipy), 8.71 (ddd, 1, $^3J_{34} = 7.8$, $^4J_{35} = 2.1$, $^5J_{36} = 0.9$ Hz, bipy), 8.52 (dt, 1, $J = 9.0$, $^4J_{4'6'} = 1.5$ Hz, bipy), 8.45 (ddd, $^3J_{3'4'} = 8.1$, $^4J_{3'5'} = 0.9$, $^5J_{3'6'} = 0.9$ Hz, bipy), 8.10 (dt, $J = 8.0$, $^3J_{46} = 1.4$ Hz, bipy), 7.93 (ddd, 1, $^3J_{5'6'} = 8.7$, $^3J_{5'4'} = 6.0$, $^4J_{5'3'} = 1.2$ Hz, bipy), 7.38 (ddd, 1, $^3J_{54} = 7.5$, $^3J_{56} = 5.7$, $^5J_{53} = 1.2$ Hz, bipy), 7.05 (ddd, 1, $^3J_{6'5'} = 5.6$, $^4J_{6'4'} = 1.2$, $^5J_{6'3'} = 0.9$ Hz, bipy), 3.72 (dq, 2, $^2J_{HH} = 16$, $^3J = 7.6$ Hz, CH_2CH$_3$), 3.45 (dq, 2, $^2J_{HH} = 17$, $^3J_{HH} = 7.3$ Hz, CH_2CH$_3$), 1.90 (s, 6, Re*Me*), 1.56 (t, 6, $J_{HH} = 7.5$ Hz, CH$_2$CH_3). ^{13}C{^{1}H} (CD_3CN): δ 159, 153, 152, 150, 148, 144, 141, 129.13, 129.06, 127, 126, 24.4 (Re*Me*), 21.7 (*C*H$_2$CH$_3$), 14.1 (CH$_2$*C*H$_3$). IR (KBr, Nujol, cm^{-1}): 1609 s, 1574 m, 1490 m, 1321 s, 1242 m, 1165 m, 1111 m, 1078 m, 1047 m, 1034 m, 970 s, 895 m, 837 vs, 771 s, 733 m.

4.4. *trans*-[$ReOMe_2(bipy)(PhCCPh)][PF_6]$ (**1d**)

To a green solution of [$ReOMe_2(bipy)(CH_3CN)$]-[PF_6], prepared in situ from $ReOMe_2(bipy)Cl$ (0.080 g, 0.19 mmol) and $AgPF_6$ (0.045 mg, 0.18 mmol) in CH_3CN (15 ml), was added diphenylacetylene (0.037 g, 0.21 mmol). The red mixture was stirred for 10 h and then filtered. The filtrate was taken to dryness in vacuo,

and the residue was washed with benzene (2 × 5 ml). The residual dark powder was dissolved in CH_2Cl_2 (5 ml) and then layered with hexanes (15 ml). After 1 day at r.t., golden yellow crystals appeared (yield 0.060 g, 45%). Anal. Calc. for $C_{26}H_{24}N_2ORePF_6$: C, 43.88; H, 3.40; N, 3.94. Found: C, 43.56; H, 3.29; N, 3.94%.

^{1}H-NMR (CD_2Cl_2): δ 9.56 (d, 1, J_{HH} = 5.7 Hz, bipy), 8.77 (d, 1, J_{HH} = 8.4 Hz, bipy), 8.56 (dt, 1, J_{HH} = 8.1, J_{HH} = 1.2 Hz, bipy), 8.49 (d, 1, J_{HH} = 8.1 Hz, bipy), 8.10 (dt, 1, J_{HH} = 8.1, J_{HH} = 1.0 Hz, bipy), 7.96 (dt, 1, J_{HH} = 6.3, J_{HH} = 1.0 Hz, bipy), 7.77 (d, 2, J_{HH} = 7.5 Hz, *Ph*CC*Ph*), 7.68 (t, 2, J_{HH} = 7.5 Hz, *Ph*CC*Ph*), 7.55 (t, 1, J_{HH} = 7.5 Hz, *Ph*CC*Ph*), 7.50 (dt, 1, J_{HH} = 7.2, J_{HH} = 1.1 Hz, bipy), 7.41 (d, 1, J_{HH} = 5.1 Hz, bipy), 1.97 (s, 6, Re*Me*). ^{13}C{^{1}H} (CD_2Cl_2): δ 158, 153, 152, 151, 149, 147, 146.6, 144, 141, 132, 131, 129.9, 129.8, 128.8, 128.5, 127, 126, 29.8 (Re*Me*). IR (KBr, Nujol, cm^{-1}): 1606 s, 1321 s, 1033 m, 972 s, 837 vs, 598 s, 559 s.

4.5. *trans-[ReOMe$_2$(bipy)(HCCMe)][PF$_6$]* (**1e**)

This compound was prepared by a procedure analogous to the one used to prepare **1a**. The compound was isolated as greenish–yellow crystals (yield 40%). Anal. Calc. for $C_{15}H_{18}N_2ORePF_6$: C, 31.42; H, 3.16; N, 4.92. Found. C, 31.40; H, 3.16; N, 4.88%.

^{1}H-NMR (CD_2Cl_2): δ 10.36 (s, 1, *H*CCMe), 9.42 (d, 1, J_{HH} = 6.0 Hz, bipy), 8.70 (d, 1, J_{HH} = 8.1 Hz, bipy), 8.53 (dt, 1, J_{HH} = 7.8, J_{HH} = 1.2 Hz, bipy), 8.42 (d, 1, J_{HH} = 8.4 Hz, bipy), 8.09 (dt, 1, J_{HH} = 7.5, J_{HH} = 1.2 Hz, bipy), 7.89 (dt, 1, J_{HH} = 6.9, J_{HH} = 1.2 Hz, bipy), 7.39 (dt, 1, J_{HH} = 6.9, J_{HH} = 1.8 Hz, bipy), 7.04 (d, 1, J_{HH} = 5.7 Hz, bipy), 3.36 (d, 3, $^4J_{HH}$ = 1.5 Hz, HCC*Me*), 2.19 (s, 3, Re*Me*), 1.98 (s, 3, Re*Me*). ^{13}C{^{1}H} (CD_2Cl_2): δ 159, 153, 149, 147, 146, 143, 141, 130, 129, 128, 127, 125, 26.7 (Re*Me*), 24.0 (Re*Me*), 13.0 (HCC*Me*). IR (KBr, Nujol, cm^{-1}): ν(C≡C) 1770 w, 1606 sh, 1406 m, 1321 s, 1155 m, 1113 m, 1052 m, 1024 m, 976 s, 900 s, 839 s, 768 s, 733 s, 557 s.

4.6. *trans-[ReOMe$_2$(bipy)(PhCCH)][PF$_6$]* (**1f**)

This compound was prepared by a procedure analogous to the one used to prepare **1c**. The compound was isolated as a dark blue powder (yield 61%). Anal. Calc. for $C_{20}H_{20}N_2ORePF_6$: C, 37.80; H, 3.17; N, 4.40. Found. C, 37.36; H, 2.86; N, 4.30%.

^{1}H-NMR (CD_2Cl_2): δ 10.86 (s, 1, *H*CCPh), 9.50 (d, 1, J_{HH} = 5.7 Hz, bipy), 8.77 (d, 1, J_{HH} = 8.1 Hz, bipy), 8.55 (dt, 1, J_{HH} = 7.8, J_{HH} = 1.0 Hz, bipy), 8.48 (d, 1, J_{HH} = 8.1 Hz, bipy), 8.10 (dt, 1, J_{HH} = 8.0, J_{HH} = 1.1 Hz, bipy), 7.92 (dt, 1, J_{HH} = 6.9, J_{HH} = 1.5 Hz, bipy), 7.89 (m, 2, *Ph*CCH), 7.69 (m, 2, *Ph*CCH), 7.62 (m, 1, *Ph*CCH), 7.42 (dt, 1, J_{HH} = 6.8, $^2J_{HH}$ = 1.3 Hz, bipy), 7.30 (d, 1, J_{HH} = 5.4 Hz, bipy), 2.33 (s, 3, Re*Me*), 1.83 (s, 3, Re*Me*). ^{13}C{^{1}H} (CD_3CN): δ 32.0 (Re*Me*), 22.6 (Re*Me*). IR (KBr, Nujol, cm^{-1}): ν(C≡C) 1765 w, 1605 sh, 1319 s, 1165 m, 1111 m, 1076 m, 1022 m, 979 s, 947 w, 837 vs, 767 s, 731 s.

4.7. *[Re{C[C(O)OMe]C(Me)C(O)(OMe)}(O)Me(bipy)][PF$_6$]* (**2**)

To a green solution of [$ReOMe_2$(bipy)(CH_3CN)][PF_6], prepared in situ from $ReOMe_2$(bipy)Cl (0.080 g, 0.19 mmol) and $AgPF_6$ (0.048 mg, 0.19 mmol) in CH_2Cl_2–CH_3CN (15–0.5 ml), was added dimethyl acetylenedicarboxylate (24 μl, 0.20 mmol). The red mixture was stirred for 2 days, and then filtered. The filtrate was taken to dryness in vacuo, and the residue was washed with benzene (2 × 5 ml) and diethyl ether (2 × 10 ml). The residual dark powder was dissolved in CH_2CL_2 (5 ml) and then layered with hexanes (15 ml). After 3 days at r.t., the compound was isolated as dark purple crystals (yield 0.074 g, 58%). A satisfactory analysis was not obtained. Anal. Calc. for $C_{18}H_{20}N_2O_5RePF_6$: C, 32.00; H, 2.98; N, 4.15. Found: C, 29.07; H, 2.87; N, 4.13%.

^{1}H-NMR (CD_3CN): δ 9.73 (d, 1, J_{HH} = 5.7 Hz, bipy), 9.58 (d, 1, J_{HH} = 5.4 Hz, bipy), 8.75 (dt, 1, J_{HH} = 8.1, J_{HH} = 1.2 Hz, bipy), 8.68 (d, 1, J_{HH} = 8.1 Hz, bipy), 8.59 (m, 1, bipy), 8.45 (m, 1, bipy), 8.17 (m, 1, bipy), 8.00 (m, 1, bipy), 3.90 (s, 3, *Me*), 3.40 (s, 3, *Me*), 3.21 (s, 3, *Me*), 2.63 (s, 3, *Me*). ^{13}C{^{1}H} (CD_3CN): δ 197 (C_α), 178, 176, 160, 158.4, 157.6, 154, 147, 145, 130.7, 129.6, 125.7, 125.5, 124.5, 55.6 (O*Me*), 53.1 (O*Me*), 13.8, 11.6. IR (KBr, Nujol, cm^{-1}): 1713 s, 1606 s, 1597 s, 1246 s, 1167 w, 1111 w, 1047 m, 1022 s, 841 vs, 770 s, 729 m.

4.8. *cis-[ReOMe$_2$(bipy){C(H)CH(PMe$_3$)}][PF$_6$]* (**3a**)

Compound **1a** (0.10 g, 0.18 mmol) was dissolved in CH_2Cl_2 (30 ml). The purple solution was frozen, and PMe_3 (0.20 mmol) was added to the flask via a calibrated vacuum manifold. The solution was allowed to warm to r.t., whereupon the color changed to dark red. The mixture was stirred for 3 h and then filtered. The solvent was removed in vacuo from the filtrate, and the dark red residue was washed with diethyl ether (2 × 25 ml). The residue was extracted with CH_2Cl_2 (2 × 10 ml), and the extracts were filtered. The filtrates were combined and then reduced in volume to approximately 10 ml. The solution was layered with hexanes (30 ml). The product formed as a dark red powder at r.t. as the layers mixed (yield 0.010 g, 45%). Anal. Calc. for $C_{17}H_{25}N_2ORePF_6$: C, 32.13; H, 3.96; N, 4.41. Found: C, 32.25; H, 3.95; N, 3.93.

^{1}H-NMR (CD_3CN): δ 11.1 (dd, 1, J_{HH} = 17.1, J_{PH} = 33.0 Hz, ReC*H*CHP), 9.00 (dd, 1, J_{HH} = 6.3, J_{HH} = 1.7 Hz, bipy), 8.53 (dd, 1, J_{HH} = 8.4, J_{HH} = 1.6 Hz, bipy),

8.26 (dd, 1, $J_{HH} = 8.7$, $J_{HH} = 1.2$ Hz, bipy), 8.05–7.88 (m, 3, bipy), 7.60 (ddd, 1, $J_{HH} = 7.2$, $J_{HH} = 4.5$, $J_{HH} = 1.4$ Hz, bipy), 7.39 (dt, 1, $J_{HH} = 8.4$, $J_{HH} = 1.6$ Hz, bipy), 3.74 (dd, 1, $J_{HH} = 17.1$, $J_{PH} = 31.8$ Hz, ReCHC*H*P), 3.04 (s, 3, Re*Me*), 2.01 (s, 3, Re*Me*), 1.52 (d, 1, $J_{PH} = 14.1$ Hz, P*Me*$_3$). $^{13}C\{^1H\}$ (CD_3CN): δ 192 (d, $J_{CP} = 11$ Hz, Re*C*HCHP), 153, 151, 150, 147, 141, 139, 127, 126, 125, 124, 105 (d, $J_{CP} = 81$ Hz, ReCH*C*HP), 19.0 (Re*Me*), 16.8 (Re*Me*), 11.4 (d, $J_{CP} = 58$ Hz, P*Me*$_3$). $^{31}P\{^1H\}$ (CD_3CN): δ 9.5. IR (KBr, Nujol, cm^{-1}): 1607 s, 1584 w, 1572 w, 1499 m, 1315 m, 1302 s, 1265 w, 1242 w, 1165 m, 1135 m, 978 s, 875 s, 841 vs, 766 s, 557 s.

4.9. *cis*-[ReOMe$_2$(bipy){C(H)CH(PPh$_3$)}][PF$_6$] (**3b**)

Compound **1a** (0.11 g, 0.20 mmol) was dissolved in CH_2Cl_2 (30 ml), yielding a purple solution. PPh_3 (0.050 g, 0.20 mmol) was added, and the solution turned to red immediately. The mixture was stirred for 3 h and then filtered. The solvent was removed from the filtrate in vacuo, and the dark red residue was washed with diethyl ether (2×25 ml). The residue was extracted with CH_2Cl_2 (2×10 ml), and the extracts were filtered through a Celite pad. The filtrates were combined, and the volume was reduced in vacuo to approximately 10 ml. The solution was layered with hexanes (30 ml). The compound precipitated as a dark powder as the layers mixed (yield 0.10 g, 62%). Anal. Calc. for $C_{32}H_{31}N_2ORePF_6$: C, 46.77; H, 3.88; N, 3.41. Found: C, 46.52; H, 4.01; N, 3.01%.

^{1}H-NMR (CD_3CN): δ 11.15 (dd, 1, $J_{HH} = 17.0$, $J_{PH} = 32.0$ Hz, ReC*H*CHP), 8.95 (d, 1, $J_{HH} = 5.7$ Hz, bipy), 8.56 (d, 1, $J_{HH} = 7.8$ Hz, bipy), 8.30 (d, 1, $J_{HH} = 8.4$ Hz, bipy), 8.09 (d, 1, $J_{HH} = 5.7$ Hz, bipy), 7.99 (m, 2, bipy), 7.83–7.22 (m), 4.30 (dd, 1, $J_{HH} = 16.8$, $J_{PH} = 31$ Hz, ReCHC*H*P), 3.07 (s, 3, Re*Me*), 2.06 (s, 3, Re*Me*). $^{13}C\{^1H\}$ (CD_3CN): δ 204 (d, $J_{CP} = 9.8$ Hz, Re*C*HCHP), 98.4 (d, $J_{CP} = 83$ Hz ReCH*C*HP), 19.6 (Re*Me*), 18.7 (Re*Me*). $^{31}P\{^1H\}$ (CD_3CN): δ 12.3. IR (KBr, Nujol, cm^{-1}): 1605 m, 1315 w, 1263 w, 1242 w, 1161 w, 1111 s, 1026 w, 983 s, 839 vs, 768 s, 746 m, 725 s, 692 m, 588 s, 517 s.

4.10. *cis*-[ReOMe$_2$(bipy){C(Ph)CH(PMe$_3$)}][PF$_6$] (**3c**)

Compound **1a** (0.10 g, 0.18 mmol) was dissolved in CH_2Cl_2 (30 ml). The purple solution was frozen, and PMe_3 (0.20 mmol) was added to the flask via a calibrated vacuum manifold. The solution was allowed to warm to r.t., whereupon the color turned to dark red. The mixture was stirred for 3 days and then filtered. The solvent was removed from the filtrate in vacuo. The dark red residue was washed with diethyl ether (2×25 ml), and then extracted with CH_2Cl_2 (2×10 ml). The extracts were combined and filtered, and the filtrate volume was reduced in vacuo to approximately 10 ml. The solution was layered with hexanes (30 ml). The compound precipitated as a dark powder as the layers mixed (yield 0.060 g, 90%).

^{1}H-NMR (CD_3CN): δ 8.7 (d, 1, $J_{HH} = 5.7$ Hz, bipy), 8.6 (d, 1, $J_{HH} = 7.8$ Hz, bipy), 8.30 (d, 1, $J_{HH} = 8.4$ Hz, bipy), 7.94 (m), 7.6 (m), 7.4–7.1 (m), 6.20 (d, $J_{HH} = 7.5$ Hz), 3.69 (d, 1, $J_{HP} = 29.1$ Hz, ReC(Ph)C*H*P), 3.40 (s, 3, Re*Me*), 2.18 (s, 3, Re*Me*), 1.13 (d, $J_{HP} = 14.1$ Hz, PMe_3). $^{13}C\{^1H\}$ (CD_3CN): δ 217 (d, $J_{CP} = 12$ Hz Re*C*(Ph)CHP), 153, 152, 150, 147, 141, 139, 129.5, 128.5, 127.8, 127.1, 126, 125.3, 125.2, 124.4, 124.3, 124.2, 103 (d, $J_{CP} = 78$ Hz, ReC(Ph)*C*HP), 22.6 (Re*Me*), 13.8 (Re*Me*), 13.7 (d, $J_{CP} = 56.1$ Hz, ReC(Ph)CHP*Me*$_3$). $^{31}P\{^1H\}$ (CD_3CN): δ 5.76. IR (KBr, Nujol, cm^{-1}): 1607 m, 1505 w, 1300 s, 1263 w, 1244 w, 1157 m, 1136 m, 978 s, 959 s, 839 vs, 766 s.

4.11. Kinetics studies

The isomerization of *cis*- to *trans*-[ReOMe$_2$(bipy)(alkyne)][PF$_6$] was monitored by ^{1}H-NMR spectroscopy. For each kinetics run, [ReOMe$_2$(bipy)(CH$_3$CN)][PF$_6$] was generated directly in the NMR tube by reacting ReOMe$_2$(bipy)Cl with $AgPF_6$ using a 0.02 M solution of C_6Me_6 in acetonitrile-d_3 as the solvent. A slight excess of alkyne (1.5–2 equivalents) was then added to the NMR tube via syringe or calibrated vacuum line. In all cases, the reactions to form the alkyne complexes were complete by the time the first spectrum could be recorded. Concentrations of the *cis* and *trans* isomers were determined periodically by integrating the Re–*Me* resonances versus the C_6Me_6 internal standard. The initial concentration of *cis*-[ReOMe$_2$(bipy)(alkyne)][PF$_6$], which varied between 0.02 and 0.04 M, was assumed to be equal to the sum of the concentrations of the *cis* and *trans* isomers in the first recorded spectrum. The rate constants based on the disappearance of *cis*-[ReOMe$_2$(bipy)(alkyne)][PF$_6$] at 21.5°C were 3.07 (2-butyne), 2.43 (3-hexyne), 0.672 (phenylacetylene), and 0.218 (diphenylacetylene) $\times 10^{-4}$ s^{-1}, respectively. Each rate constant represents the average of two runs; the two rate constants determined from the two different runs varied by 4–14%.

The isomerization of *cis*-**1b** to *trans*-**1b** at various temperatures was also monitored by ^{1}H-NMR spectroscopy. Solutions of *cis*-**1b** in acetonitrile-d_3, generated as described above, were cooled or heated in sealed NMR tubes directly in the probe. The initial concentrations of *cis*-**1b** varied between 0.01 and 0.02 M. The temperature was held within ± 0.1°C of 15, 20, 21.5, 25, and 30°C. The rate constants calculated from the rate of disappearance of *cis*-**1b** were 1.29, 2.33, 3.07, 4.66, and 8.55×10^{-4} s^{-1} at 15, 20, 21.5, 25 and 30°C, respectively. Each rate constant represents the average of two runs except at 15°C, where only one run was

recorded. The rate constants determined from the two runs at any one temperature differed by 2–9%. The resulting activation parameters were calculated to be $\Delta H^{\ddagger} = 21(1)$ kcal mol^{-1} and $\Delta S^{\ddagger} = 6(3)$ eu. The errors in these values were estimated from a standard linear regression analysis [20].

Rate constants based on the disappearance of *cis*-**1f** in the presence of two and ten equivalents of phenylacetylene (acetonitrile-d_3, 22°C) were 6.60 and 6.99×10^{-5} s^{-1}, respectively, and the corresponding rate constants based on the appearance of *trans*-**1f** were 5.77 and 6.88×10^{-5} s^{-1}, respectively. The rate constant based on the disappearance of *cis*-[$ReOMe_2$(bipy)(PhCCH)][CF_3SO_4] (acetonitrile-d_3, 22°C) was 6.27×10^{-5} s^{-1}, while the rate constant based on the appearance of the *trans* isomer was 6.69×10^{-5} s^{-1}. Rate constants based on the disappearance of *cis*-**1f** (acetonitrile-d_3, 22°C) in the presence of ten equivalents of bipyridine or 100 equivalents of pyridine-d_5 were, respectively, 6.45 and 7.71×10^{-5} s^{-1}, while the corresponding rate constants based on the appearance of *trans*-**1f** were, respectively, 4.42 and 1.24×10^{-5} s^{-1} (the values for the pyridine-d_5 experiments were averaged from two runs).

4.12. X-ray structure determinations

Crystals for analyses of **1d** (olive green flat plate), **2** (dark purple column), **3b**·C_7H_8 (brown tapered column), and **3c**·C_7H_8 (dark red diamond-shaped thin plate) were grown from CH_2Cl_2–hexanes at r.t. (**1d** and **2**) or toluene at −25°C (**3b**·C_7H_8 and **3c**·C_7H_8). X-ray data for **1d** were collected on a Nicolet R3m/V diffractometer, and data for the others were collected on a Siemens SMART platform diffractometer equipped with a 1K CCD area detector. The crystals were manipulated under mineral oil during the mounting procedures. Data for **1d** were collected using the $\theta - 2\theta$ scan technique.

The anion in **1d** was found to be disordered over two different orientations, which was treated by introducing two individual rigid bodies at this site and allowing independent rotation. By comparison of the isotropic thermal parameters involved, the population factors were determined to be 60:40% for the P:P′ orientations. In **3b**·C_7H_8, the toluene solvent molecule was treated as a rigid body because of disorder. The analyses of **2** and **3c**·C_7H_8 were routine.

5. Supplementary material

Crystallographic data for **1d**, **2**, **3b**·C_7H_8 and **3c**·C_7H_8 have been deposited with the Cambridge Crystallographic Data Center (CCDC nos. 135 955, 135 956, 135 958, and 135 957, respectively). Copies of this information can be obtained free from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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