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Synthesis and Reactivity of New Rhenium(I) Complexes Containing Iminophosphorane-Phosphine Ligands: Application to the Catalytic Isomerization of Propargylic Alcohols in Ionic Liquids

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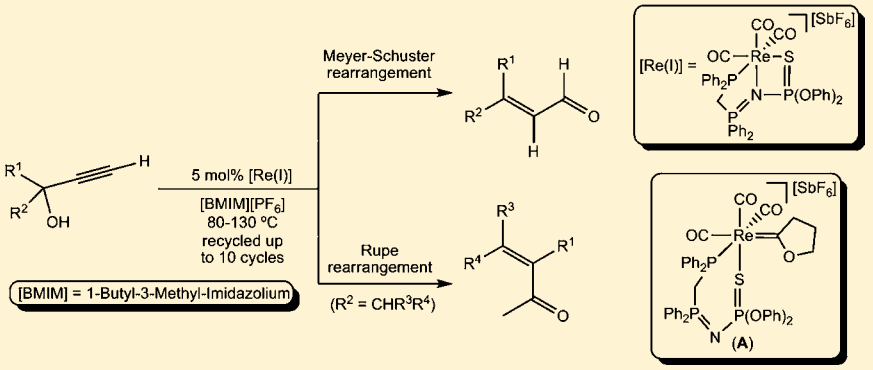
Supporting Information



ABSTRACT: $[ReBr(CO)_5]$ reacts with the iminophosphorane–phosphine ligands $Ph_2PCH_2P(=NR)Ph_2$ (R = $P(=O)(OEt)_2$ (**1a**), $P(=O)(OPh)_2$ (**1b**), $P(=S)(OEt)_2$ (**1c**), $P(=S)(OPh)_2$ (**1d**), 4-C_6F_4CHO (**1e**), 4-C_6F_4CN (**1f**), 4-C_5F_4N (**1g**)) affording the neutral complexes $[ReBr(\kappa^2\text{-}P,X\text{-}Ph_2PCH_2P\{=NP(=X)(OR)_2\}Ph_2)(CO)_3]$ (X = O, R = Et (**2a**), Ph (**2b**); X = S, R = Et (**2c**), Ph (**2d**)) and $[ReBr\{\kappa^2\text{-}P,N\text{-}Ph_2PCH_2P(=NR)Ph_2\}(CO)_3]$ (R = $P(=O)(OEt)_2$ (**3a**), $P(=O)(OPh)_2$ (**3b**), 4-C_6F_4CHO (**3e**), 4-C_6F_4CN (**3f**), 4-C_5F_4N (**3g**)). The reactivity of the cationic complex $[Re(\kappa^3\text{-}P,N,S\text{-}Ph_2PCH_2P\{=NP(=S)(OPh)_2\}Ph_2)(CO)_3][SbF_6]$ (**4d**) has been explored allowing the synthesis of the cationic $[Re(L)(\kappa^2\text{-}P,S\text{-}Ph_2PCH_2P\{=NP(=S)(OPh)_2\}Ph_2)(CO)_3][SbF_6]$ (L = acetone (**5a**), $CH_3C{\equiv}N$ (**5b**), pyridine (**5c**), PPh_3 (**5d**)) and the neutral $[ReY(\kappa^2\text{-}P,S\text{-}Ph_2PCH_2P\{=NP(=S)(OPh)_2\}Ph_2)(CO)_3]$ (Y = Cl (**6a**), I (**6b**), N_3 (**6c**)) complexes. The catalytic activity of complex **4d** in the regioselective isomerization of terminal propargylic alcohols $HC{\equiv}CCR^1R^2(OH)$ into α,β-unsaturated aldehydes $R^1R^2C{=}CHCHO$ or ketones $R^3R^4C{=}CR^1COMe$ (if $R^2 = CHR^3R^4$) under neutral conditions in ionic liquids has being studied. Isolation and X-ray characterization of the key intermediate rhenium(I) oxocyclocarbene complex $[Re\{{=}C(CH_2)_3O\}(\kappa^2\text{-}P,S\text{-}Ph_2PCH_2P\{=NP(=S)(OPh)_2\}Ph_2)(CO)_3][SbF_6]$ (**5e**) seems to indicate that the catalytic reaction proceeds through tautomerization of the terminal alkynols to yield vinylidene-type species.

INTRODUCTION

The coordination chemistry of bidentate phosphines with hemilabile properties has spurred great interest because these ligands combine the presence of a phosphorus atom (with strong metal bond) together with a more labile donor group (i.e., N atom in aminophosphines or O atom in etherphosphines). The main feature of these heteroditopic ligands stems from the ability of the "hard" N and O atoms to dissociate reversibly from a "soft" metal giving rise to a free coordination site.[1] Such behavior has been exploited in homogeneous catalysis since the formation of unsaturated intermediate species is often favored. Closely related hemilabile ligands are diphosphine monoxides of general formula $R_2P{-}Y{-}P(=O)R_2$ (Y = divalent bridging group), which have also been used as ligands in a large number of efficient catalytic transformations.[2] Iminophosphorane–phosphines of the type $Ph_2PCH_2P(=NR)Ph_2$ (readily accessible by selective monoimination of bis(diphenylphosphine)methane (dppm) with azides *via* Staudinger reaction)[3,4] are an important class of hemilabile ligands belonging to the wide series of those containing phosphorus–nitrogen donor atoms.[5] During the past decade, we have used extensively the iminophosphorane–phosphines $Ph_2PCH_2P(=NR)Ph_2$ (R = $P(=O)(OEt)_2$ (**1a**), $P(=O)(OPh)_2$ (**1b**), $P(=S)(OEt)_2$ (**1c**), $P(=S)(OPh)_2$ (**1d**), 4-C_6F_4CHO (**1e**), 4-C_6F_4CN (**1f**), 4-C_5F_4N (**1g**); see Figure 1) as ligands in a wide series of ruthenium(II)[6a−e,g] and palladium(II)[6f] complexes and studied their catalytic activity in organic reactions such as the transfer hydrogenation of

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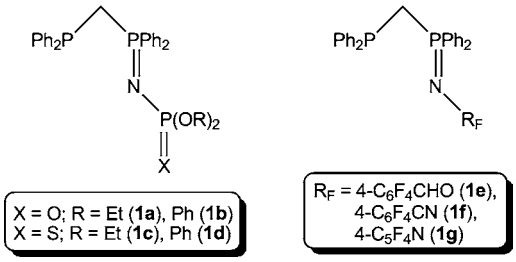

Figure 1. Iminophosphorane−phosphine ligands $Ph_2PCH_2P(=NR)Ph_2$ (**1a−g**).

ketones[6b−d] and the cycloisomerization of (*Z*)-3-methylpent-2-en-4-yn-1-ol into 2,3-dimethylfuran.[6f]

Following our interest in using this type of ligand and taking into account that ruthenium(II) and rhenium(I) are isoelectronic d^6 species and show analogous coordination chemistry,[7] we sought the synthesis of new iminophosphorane−phosphine rhenium(I) derivatives and explored their catalytic activity. In this regard, we have recently reported the first series of tricarbonyl rhenium(I) complexes **4c,d** (Figure 2), which are

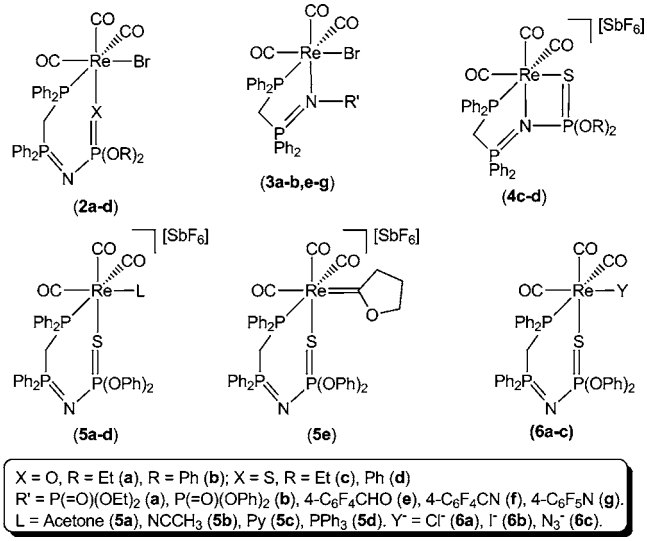

Figure 2. Structure of the rhenium(I) complexes containing iminophosphorane−phosphine ligands **1a−g**.

highly active catalysts in the isomerization of propargylic alcohols into α,β-unsaturated carbonyl compounds in THF.[8,9] Thus, continuing with these studies, herein we report a new family of rhenium(I) derivatives containing iminophosphorane-phosphine ligands, namely, complexes **2a−d**, **3a−b,e−g**, **5a−e** and **6a−c** (Figure 2). The following features can be remarkable: (*i*) First is the synthesis of complexes **5a−d** and **6a−c** (Figure 2), obtained by the reaction of the hemilabile complex **4d** with monodentate neutral and anionic ligands, respectively, which proceeds through a change of the coordination mode from k^3-*P,N,S* into k^2-*P,S*. (*ii*) Next is the synthesis of the cationic oxacyclic−carbene complex **5e**, obtained from the reaction of complex **4d** with the alkynol $HC{\equiv}C{-}CH_2{-}CH_2OH$, *via* the formation of an intermediate hydroxyvinylidene complex $[Re]^+{=}C{=}C(H)CH_2(OH)$ and followed by the intramolecular nucleophilic addition of the OH group to the carbenic carbon atom. This process sheds light on the proposed mechanism of the catalytic isomerization of propargylic alcohols. (*iii*) The high catalytic activity of complexes **4c,d** in the regio and selective isomerization of propargylic alcohols into α,β-unsaturated aldehydes (Meyer−Schuster rearrangement)[10a] or ketones (Rupe rearrangement),[10b] using ionic liquids as reaction media.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Neutral Complexes [ReBr(κ^2-*P,X*-$Ph_2PCH_2P\{=NP(=X)(OR)_2\}Ph_2$)-$(CO)_3$] (X = O, R = Et (2a), Ph (2b); X = S, R = Et (2c), Ph (2d)] and [ReBr(κ^2-*P,N*-$Ph_2PCH_2P\{=NR\}Ph_2$)$(CO)_3$] (R = P(=O)$(OEt)_2$ (3a), P(=O)$(OPh)_2$ (3b), 4-C_6F_4CHO (3e), 4-C_6F_4CN (3f), 4-C_6F_5N (3g)). As expected from our previous results,[6c] the treatment of the complex $[ReBr(CO)_5]$ with an equimolecular amount of $Ph_2PCH_2P\{=NP(=O)(OR)_2\}Ph_2$ (**1a,b**) in refluxing THF results in the formation of an inseparable mixture of the κ^2-*P,O* and κ^2-*P,N* neutral complexes $[ReBr(\kappa^2\text{-}P,O\text{-}Ph_2PCH_2P\{=NP(=O)(OR)_2\}Ph_2)(CO)_3]$ (R = Et (**2a**), Ph (**2b**)) and $[ReBr(\kappa^2\text{-}P,N\text{-}Ph_2PCH_2P\{=NP(=O)(OR)_2\}Ph_2)(CO)_3]$ (R = Et (**3a**), Ph (**3b**); see Scheme 1).[11] In contrast, under the same reaction conditions but using the *N*-thiophosphorylated iminophosphorane ligands **1c,d**, selective coordination of the diphenylphosphino (PPh_2) and thiophosphoryl group ($(RO)_2P{=}S$) to the rhenium(I) center is achieved to afford the neutral complexes $[ReBr(\kappa^2\text{-}P,S\text{-}Ph_2PCH_2P\{=NP(=S)(OR)_2\}Ph_2)(CO)_3]$ (R = Et (**2c**), Ph (**2d**)).[12] Similarly, selective formation of the κ^2-*P,N*-iminophosphorane complexes $[ReBr(\kappa^2\text{-}P,N\text{-}Ph_2PCH_2P\{=NR_F\}Ph_2)(CO)_3]$ (**3e−g**) also occurs by using the fluorinated ligands **1e−g**.[13]

Compounds **2a−d** and **3a,b,e−g** have been isolated as air-stable white solids in 82−96% yields. The characterization of these complexes (see Supporting Information) was achieved by means of standard spectroscopic techniques (^1H, $^{31}P\{^1H\}$, $^{19}F\{^1H\}$, $^{13}C\{^1H\}$ NMR and IR) as well as elemental analyses. In particular, IR spectra show the presence of three ν(CO) absorptions at 1887−2026 cm^{-1} in accordance with the *fac*-arrangement of the three carbonyl ligands. $^{31}P\{^1H\}$ NMR spectra allow the coordination mode adopted by the iminophosphorane−phosphine ligand in **2**, **3a,b** to be distinguished (see Experimental Section). Thus, for **3a,b** the κ^2-*P,N* coordination is reflected in an important downfield shift of both the PPh_2 ($\Delta\delta_P$ *ca.* 27 ppm) and $Ph_2P{=}N$ ($\Delta\delta_P$ *ca.* 40 ppm) signals with respect to those found in the free ligands **1a−b**,[6c] while the κ^2-*P,O* coordination in complexes **2a,b** is revealed in (*i*) an appreciable downfield shift only in the PPh_2 ($\Delta\delta_P$ *ca.* 27 ppm) signals and (*ii*) a slightly downfield shift for resonances of the $(RO)_2P{=}O$ signal ($\Delta\delta_P$ *ca.* 5 ppm), in comparison with those found in the free ligands **1a,b**,[6c] confirming the direct involvement of these groups in the bonding to the metallic center. Concerning complexes **2c,d**, downfield shifts are also observed for the Ph_2P signals with respect to the free iminophosphorane−phosphine ligands **1c,d** ($\Delta\delta_P$ *ca.* 26 ppm).[6d] This fact along with the slight high-field shifting of the $(RO)_2P{=}S$ resonances ($\Delta\delta_P$ *ca.* 4 ppm, similar to those previously observed in the *S*-coordination of the unit $-P{=}N{-}P(=S)(OR)_2$ to Au(I),[14] Ag(I),[15] Cu(I),[16] Ru(II),[17] and Pd(II)[18] fragments), allows us to propose that, in this case, rhenium complexation takes place selectively on the $(RO)_2P{=}S$ vs $Ph_2P{=}N$ groups. Finally, for complexes **3e−g**, selective κ^2-*P,N* coordination of the PPh_2 ($\Delta\delta_P$ *ca.* 37 ppm) and $Ph_2P{=}N$ ($\Delta\delta_P$ *ca.* 40 ppm) groups is observed. ^1H and $^{13}C\{^1H\}$ NMR spectra exhibit signals in accordance with the proposed formulations, the most significant features being those

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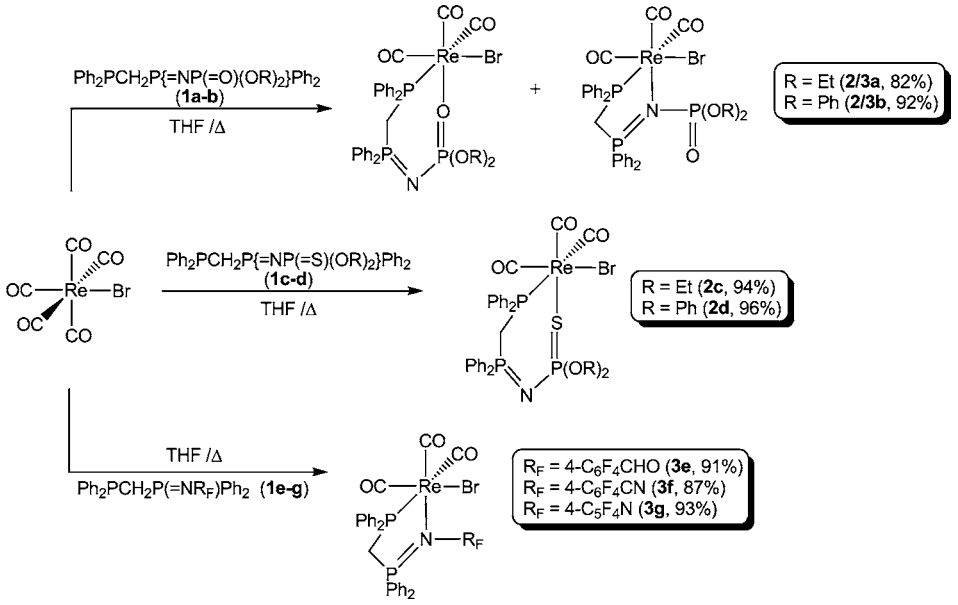
Scheme 1. Synthesis of the Neutral Re(I) Complexes 2−3



concerning the methylenic PCH_2P group of the ligands **1a−g**: (*i*) in the ^1H NMR, two unresolved multiplet signals at 3.40−5.88 ppm for **2a−d** and **3a,b,e−g** and (*ii*) in the $^{13}C\{^1H\}$ NMR, a characteristic doublet of doublets in the range of 22.90−28.35 ppm (J_{CP} = 79.4−10.8 Hz) for **3b,e-g** and **2c,d**; a doublet of doublets of doublets at 33.11 ppm (J_{CP} = 78.7 and 12.9 Hz, $^3J_{CP}$ = 9.6 Hz) for **2b**; and one unresolved multiplet signal at 30.08 ppm for the mixture of compounds **2**,**3a**.

Moreover, the structure of the complex [Re(κ^2-*P,N*-$Ph_2PCH_2P\{=N(4\text{-}C_6F_4CHO)\}Ph_2$)$(CO)_3$] (**3e**) was unambiguously confirmed by means of a single-crystal X-ray diffraction study. An ORTEP-type view of the molecule is shown in Figure 3; selected bond distances and angles are listed in the caption. The geometry around the metal is slightly distorted octahedral (see values of the P(2)−Re−N(1), P(2)−Re−Br(1), N(1)−Re−Br(1), and those containing the C atoms of the carbonyl ligands), being bonded to three carbon monoxide molecules, the nitrogen atom of the iminophosphoranyl group, the phosphorus atom of the diphenylphosphino unit, and a bromine atom. The Re−P(2), Re−N(1), and Re−Br(1) bond distances in complex **3e** are in a good agreement with those previously described for other tricarbonyl−Re(I) complexes containing iminophosphorane−phosphine ligands (Re−P = 2.453(3) Å; Re−N = 2.20(1) Å; Re−Br = 2.548(2) Å).[9]

Reactivity of the Cationic Complex [Re(κ^3-*P,N,S*-$Ph_2PCH_2P\{=NP(=S)(OPh)_2\}Ph_2$)$(CO)_3$][$SbF_6$] (4d) toward Neutral and Anionic Ligands. We have recently reported that the high catalytic activity of complex [Re(κ^3-*P,N,S*-$Ph_2PCH_2P\{=NP(=S)(OPh)_2\}Ph_2$)$(CO)_3$][$SbF_6$] (**4d**) in the isomerization of propargylic alcohols into carbonyl derivatives stems from the lability of the Re−N bond, giving rise to the κ^2-*P,S* coordination mode of the ligand.[8] This fact provides the required free coordination site on the metal allowing the coordination of the propargylic C≡C bond. In order to assesses the generality of this behavior, we set out the synthesis of κ^2-*P,S* iminophosphorane complexes **5a−d** by the reaction of complex **4d** with two electron ligands.[19]

*a. Synthesis and Characterization of the Cationic Complexes [Re(L)(κ^2-P,S-$Ph_2PCH_2P\{=NP(=S)(OPh)_2\}Ph_2$)-$(CO)_3$][$SbF_6$] (L = Me_2C=O (**5a**), CH_3CN (**5b**), pyridine (**5c**), PPh_3 (**5d**)).* We found that just by dissolving the cationic complex **4d** in acetone, the solvato-complex [Re(κ^1-*O*-Me_2C=O)(κ^2-*P,S*-$Ph_2PCH_2P\{=NP(=S)(OPh)_2\}Ph_2$)$(CO)_3$][$SbF_6$] (**5a**) was readily obtained as inferred by its $^{31}P\{^1H\}$ NMR spectrum (shielding in the Ph_2P=N group resonance of *ca.* 35 ppm was observed, see Experimental Section), which clearly indicates the selective cleavage of the Re−N bond and concomitant coordination of the acetone to the rhenium center (see Scheme 2). All attempts to isolate this solvato complex failed, leading instead to its precursor **4d** quantitatively after evaporation of the solvent. The reversibility of this process evidences clearly the hemilability of the P=N unit in complex

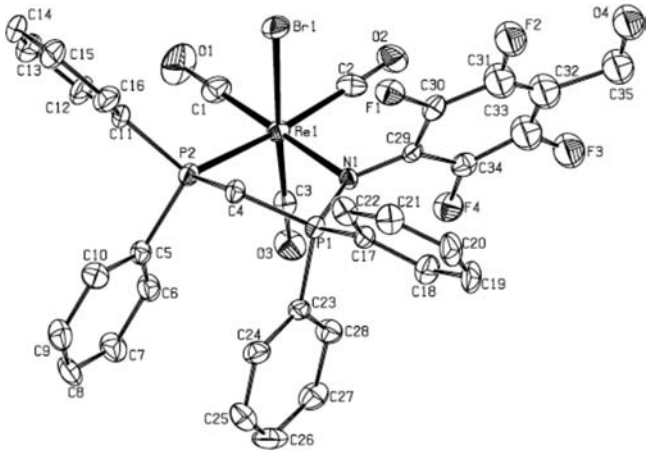


Figure 3. ORTEP-type view of the structure of the complex [ReBr(κ^2-*P,N*-$Ph_2PCH_2P\{=N(4\text{-}C_6F_4CHO)\}Ph_2$)$(CO)_3$] (**3e**) showing the crystallographic labeling scheme. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 20% probability level. Selected bond lengths (Å) and angles (deg): Re−P(2) = 2.477(2); Re−N(1) = 2.268(5); Re−Br(1) = 2.622(1); Re−C(1) = 1.87(1); Re−C(2) = 1.96(1); Re−C(3) = 1.892(9); P(2)−C(4) = 1.857(7); C(4)−P(1) = 1.788(7); P(1)−N(1) = 1.614(5); P(2)−Re−N(1) = 83.5(1); P(2)−Re−Br(1) = 83.12(5); N(1)−Re−Br(1) = 85.4(1); C(1)−Re−C(2) = 89.2(4); C(2)−Re−C(3) = 88.9(3); C(1)−Re−C(3) = 88.7(4); C(3)−Re−Br(1) = 176.3(2).

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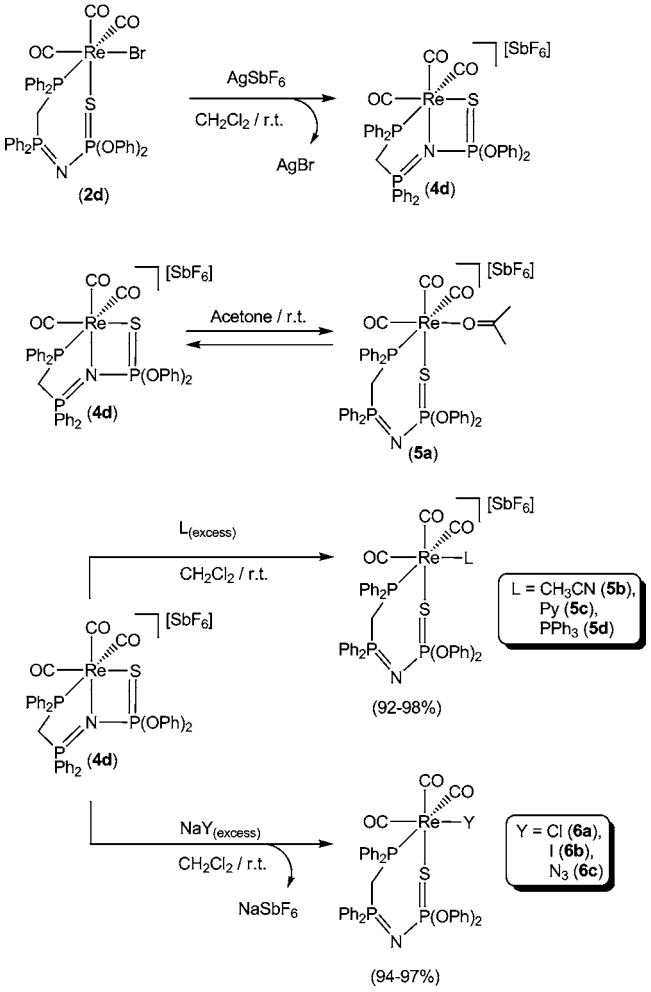
Scheme 2. Reactivity of Complex 4d Towards Neutral and Anionic Ligands



4d.[20] In contrast, for other neutral ligands such as acetonitrile (**5b**), pyridine (**5c**), or triphenylphosphine (**5d**), a lack of reversibility in the Re−N bond cleavage was observed. The results obtained are summarized in Scheme 2. Complexes **5b**−**d**, isolated as air-stable white solids in 92−98% yields, formally result from the opening of the κ^2-*P,N* chelate ring and concomitant coordination of the corresponding two-electron ligand to rhenium, while the Re−S bond remains intact. Characterization of complexes **5b**−**d** was straightforward, following their analytical and spectroscopic data (details are given in the Experimental Section and the Supporting Information). In particular, the κ^2-*P,S* coordination of the *N*-thiophosphorylated ligand is fully supported by the $^{31}P\{^1H\}$ NMR (see Experimental Section), and as previously seen for the unstable solvato complex **5a**, a remarkable shielding in the $Ph_2P{=}N$ group resonance (δ_P 14.79−16.23 ppm) with respect to that shown by the parent compound **4d** (δ_P 50.13 ppm) was observed. In contrast, the diphenylphosphino Ph_2P and thiophosphoryl $(EtO)_2P{=}S$ units are considerably less affected by the coordination of the incoming ligand (δ_P −1.13−4.02 vs 13.46 ppm; and 43.10−44.91 vs 50.13 ppm, respectively).

Moreover, the structure of the acetonitrile adduct $[Re(\kappa^1\text{-}N\text{-}NCCH_3)(\kappa^2\text{-}P,S\text{-}Ph_2PCH_2P\{{=}NP(=S)(OPh)_2\}Ph_2)(CO)_3][SbF_6]$ (**5b**) was unambiguously determined by means of a single-crystal X-ray diffraction study. An ORTEP-type drawing of the molecular structure is depicted in Figure 4. The rhenium atom is in a slightly distorted octahedral environment, being

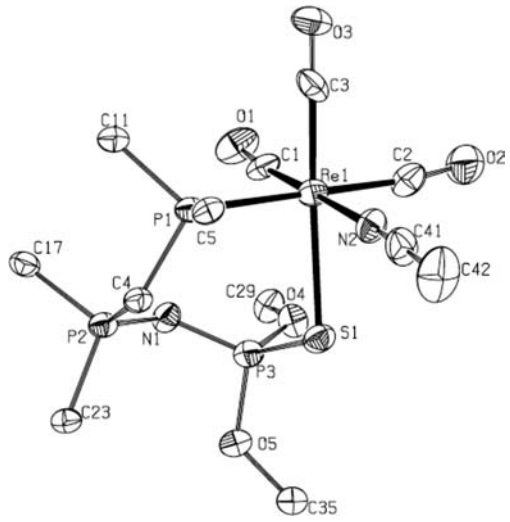


Figure 4. ORTEP-type view of the structure of the cation $[Re(\kappa^1\text{-}N\text{-}NCCH_3)(\kappa^2\text{-}P,S\text{-}Ph_2PCH_2P\{{=}NP(=S)(OPh)_2\}Ph_2)(CO)_3]^+$ of **5b** showing the crystallographic labeling scheme. Hydrogen atoms are omitted for clarity, and only the *ipso*-carbons of the phenyl rings are shown. Thermal ellipsoids are drawn at the 20% probability level. Selected bond lengths (Å) and angles (deg): Re−P(1) = 2.469(3); Re−N(2) = 2.138(9); Re−S(1) = 2.553(3); Re−C(1) = 1.89(1); Re−C(2) = 1.91(2); Re−C(3) = 1.91(1); P(1)−C(4) = 1.83(1); C(4)−P(2) = 1.836(9); P(2)−N(1) = 1.587(9); N(1)−P(3) = 1.556(9); P(3)−S(1) = 1.978(4); N(2)−C(41) = 1.14(1); C(41)−C(42) = 1.47(2); N(2)−Re−P(1) = 87.4(3); N(2)−Re−S(1) = 80.5(3); P(1)−Re(1)−S(1) = 89.45(9); C(1)−Re−C(2) = 87.2(5); C(1)−Re−C(3) = 88.4(5); C(2)−Re−C(3) = 90.2(6); Re−C(1)−O(1) = 174.0(9); Re−C(2)−O(2) = 173.1(9); Re−C(3)−O(3) = 178.1(9); Re−N(2)−C(41) = 177.0(1).

bonded to three carbon monoxide molecules, the sulfur atom of the *N*-thiophosphorylated group, the phosphorus atom of the diphenylphosphino unit, and the nitrogen atom of the acetonitrile ligand. As expected, all the carbon monoxide ligands and the acetonitrile molecule are bounded to rhenium in a nearly linear fashion [Re−C−O and Re−N−C angles within the range 173.1(9)−178.0(9)°], with metal carbon distances (Re−C) of 1.89(1)−1.92(2) Å and a Re−N bond length of 2.138(9) Å. These bonding parameters fit well with those reported in the literature for other tricarbonyl−acetonitrile−rhenium(I) complexes.[9a] Both Re−P(1) (2.469(3) Å) and Re−S(1) (2.553(3) Å) distances are in good agreement with those found in complex **4c**.[8]

b. Synthesis and Characterization of the Neutral Complexes $[ReY(\kappa^2\text{-}P,S\text{-}Ph_2PCH_2P\{{=}NP(=S)(OPh)_2\}Ph_2)(CO)_3]$ *(Y = Cl (**6a**), I (**6b**), N_3 (**6c**)).* The ability shown by the iminophosphorane $Ph_2P{=}N$ unit in complex **4d** to be displaced by neutral ligands prompted us to study the lability of the Re−N bond but using, in this case, anionic ligands. The results obtained with typical anionic ligands such as Cl^-, I^-, and N_3^- are summarized in Scheme 2. Thus, we found that the treatment of dichloromethane solutions of **4d** with an excess (*ca.* 10 equiv., see Scheme 2) of the corresponding sodium salts NaCl, NaI, and NaN_3, at room temperature, results in the selective formation of complexes $[ReY(\kappa^2\text{-}P,S\text{-}Ph_2PCH_2P\{{=}NP(=S)(OPh)_2\}Ph_2)(CO)_3]$ (Y = Cl (**6a**), I (**6b**), N_3 (**6c**)), *via* selective Re−N bond cleavage. Complexes **6a**−**c** could be

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isolated in pure form in 94−97% yield and were analytically and spectroscopically characterized (see Experimental Section and Supporting Information). The bidentate κ^2-*P*,*S* coordination of the iminophosphorane−phosphine ligand **1d** was clearly evidenced by the $^{31}P\{^1H\}$ spectrum, showing characteristic doublet signals at *ca.* 15 ppm assigned to the noncoordinated $Ph_2P{=}N$ unit (see Experimental Section).

The structure of complex $[ReCl(\kappa^2\text{-}P,S\text{-}Ph_2PCH_2P\{{=}NP({=}S)(OPh)_2\}Ph_2)(CO)_3]$ (**6a**) was unambiguously confirmed by means of a single-crystal X-ray diffraction study. An ORTEP-type view of the molecule is shown in Figure 5;

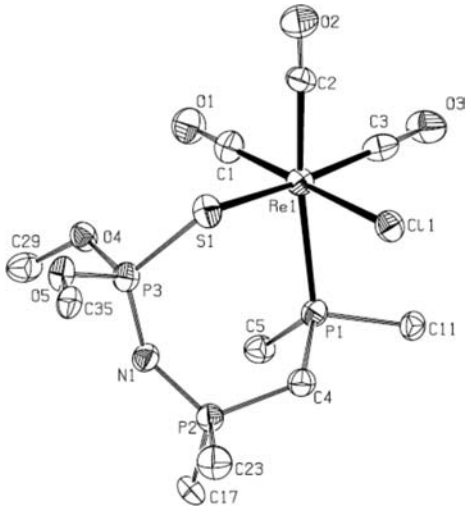
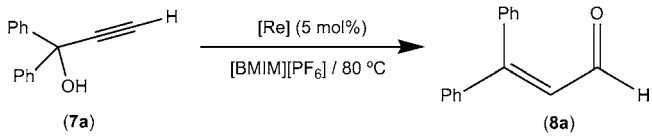


Figure 5. ORTEP-type view of the structure of the complex $[ReCl(\kappa^2\text{-}P,S\text{-}Ph_2PCH_2P\{{=}NP({=}S)(OPh)_2\}Ph_2)(CO)_3]$ (**6a**) showing the crystallographic labeling scheme. Hydrogen atoms are omitted for clarity, and only the *ipso*-carbons of the phenyl rings are shown. Thermal ellipsoids are drawn at the 20% probability level. Selected bond lengths (Å) and angles (deg): Re−P(1) = 2.494(4); Re−Cl(1) = 2.484(4); Re−S(1) = 2.532(4); Re−C(1) = 1.91(2); Re−C(2) = 1.99(2); Re−C(3) = 1.94(2); P(1)−C(4) = 1.84(2); C(4)−P(2) = 1.79(2); P(2)−N(1) = 1.58(1); N(1)−P(3) = 1.56(1); P(3)−S(1) = 1.977(6); Cl(1)−Re−P(1) = 81.3(1); Cl(1)−Re−S(1) = 81.6(2); P(1)−Re(1)−S(1) = 95.7(1); C(1)−Re−C(2) = 87.5(8); C(1)−Re−C(3) = 89.4(8); C(2)−Re−C(3) = 85.6(7); Re−C(1)−O(1) = 178.6(2); Re−C(2)−O(2) = 175.1(2); Re−C(40)−O(5) = 178.0(2).

selected bond distances and angles are listed in the caption. The geometry around the metal is slightly distorted octahedral, the Re−C, Re−P, and Re−S bond distances and interligand angles fitting well with those previously observed by us in complex **5b**, both containing the κ^2-*P*,*S* coordinated iminophosphorane−phosphine ligand **1d**. The Re−Cl bond distance (2.483(4) Å) is in a good agreement with those previously described for other tricarbonyl−Re(I) complexes.[21]

Catalytic Isomerization of Propargylic Alcohols into α,β-Unsaturated Carbonyl Compounds in Ionic Liquids. Over the past decade, there has been increasing interest in searching for new catalytic approaches using nonconventional solvents as reaction media. In this sense, a large number of organometallic catalysts have been successfully applied to a variety of organic transformations using water, supercritical CO_2, ionic liquids, glycerol, perfluorinated compounds, and low-boiling point polymers as alternative solvents to volatile organic solvents (VOCs).[22] However, and despite the growing interest in the study of the metal-catalyzed isomerization of propargylic acids into α,β-unsaturated carbonyl compounds,[23,24] efforts devoted to developing catalytic systems able to operate in nonconventional solvents, like ionic liquids, have been scare. In fact, only a very limited number of catalysts active in the Meyer−Schuster rearrangement of propargylic alcohols have been described up to now in the literature using ionic liquids as a solvent.[8,25] In this sense, and to prove the catalytic potential of complexes **2a−d**, **3a**,**b**,**e−g**, and **4c**,**d**, we decided to evaluate their catalytic activity in the isomerization of the commercially available 1,1-diphenyl-2-propyn-1-ol (**7a**) into 3,3-diphenylpropenal (**8a**) in ionic liquids as a model reaction (see Scheme 3). Thus, in a typical experiment, the

Scheme 3. Re(I)-Catalyzed Isomerization of 1,1-Diphenyl-2-propyn-1-ol (7a) into 3,3-Diphenylpropenal (8a) in [BMIM][PF$_6$][a]



(**7a**) (**8a**)

[a]Reactions were performed under a N_2 atmosphere at 80 °C, using 1 mmol of the alkynol **7a**. [Substrate]/[Re] ratio =100:5.

corresponding Re(I) precursor (5 mol % of Re) was added to a solution of the propargylic alcohol **7a** in [BMIM][PF_6] (BMIM = 1-butyl-3-methylimidazolium) at 80 °C, the course of the reaction being monitored by gas chromatography.[26] The catalytic activity of all complexes (**2a−d**, **3a**,**b**,**e−g**, and **4c**,**d**) was checked, but only the cationic complexes $[Re(\kappa^3\text{-}P,N,S\text{-}Ph_2PCH_2P\{{=}NP({=}S)(OR)_2\}Ph_2)(CO)_3][SbF_6]$ (R = Et (**4c**), Ph (**4d**)) were found to be active leading to the selective isomerization to the enal **8a** as the unique reaction product. These results are in accord with the hemilabile behavior of complexes **4c**,**d** in contrast to the inertness of the rest of the complexes toward the isomerization of the propargylic alcohol. The best result was obtained for complex **4d**, which led to the enal **8a** in quantitative yield (99%) after only 10 min of reaction vs 15 min of reaction for complex **4c**. For comparison, only 73% isomerization of the alkynol **7a** into the corresponding enal **8a** was achieved with the catalyst **4d** in a 5 mol % loading at 80 °C using conventional organic solvent (THF) after 24 h.[8]

As observed for 1,1-diphenyl-2-propyn-1-ol (entry 1, Table 1), complex **4d** was also found to be an efficient catalyst for the selective isomerization of other tertiary (entries 2−5, Table 1) and secondary (entry 6, Table 1) propargylic alcohols to the corresponding enals. It is important to note that all reactions proceeded to completion in the absence of any cocatalyst. Influence of the electronic properties of the aryl rings on the reaction rates was observed. Thus, alkynols with electron-withdrawing groups showed less reactivity (entries 2,3) as compared to the substrates with electron-donating groups (entries 4,5). Interestingly, for the secondary alcohol 1-phenyl-1-propyn-1-ol (**7f**), the resulting enal **8f** was exclusively obtained as the thermodynamically more stable *E* isomer.[27]

Nowadays it is well-known that one of the most important advantages associated with the use of ionic liquids as a solvent is the possibility of recycling the catalytic system by separation of the product of the catalytic reaction with a simple process of extraction with organic solvents.[22a] In addition, the lifetime and the level of reusability are very important factors for any catalytic system.[28] In this sense, we have studied the recyclability of catalyst **4d** in the isomerization of the

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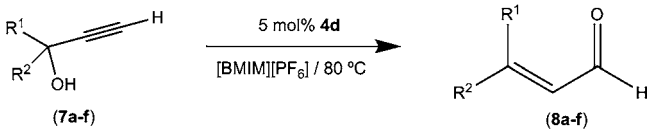
Table 1. Isomerization of Propargylic Alcohols 7a−f into Enals 8a−f Catalyzed by Complex 4d Using [BMIM][PF_6] As Solvent[a]



entry	R^1	R^2	product	time [min]	GC yield [%], isolated (%)
1	Ph	Ph	**8a**	10	99(91)
2	*p*-F(C_6H_4)	*p*-F(C_6H_4)	**8b**	15	97(94)
3	*p*-Cl(C_6H_4)	*p*-Cl(C_6H_4)	**8c**	30	99(92)
4	*p*-MeO(C_6H_4)	*p*-MeO(C_6H_4)	**8d**	10	99(94)
5	*p*-Me(C_6H_4)	*p*-Me(C_6H_4)	**8e**	5	97(94)
6	H	Ph	**8f**	15	99(93)

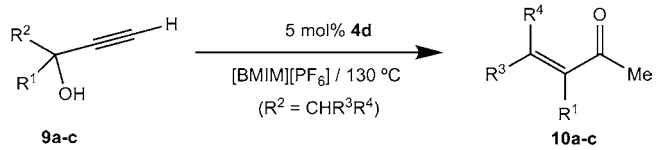
[a]Reactions were performed under a N_2 atmosphere at 80 °C, using 1 mmol of the corresponding alkynol in 1 g of [BMIM][PF_6] and with a catalyst loading of 5 mol % in Re.

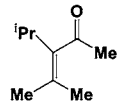
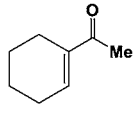
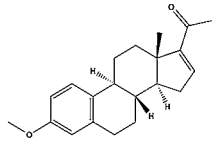
propargylic alcohols **8a−f**, using [BMIM][PF_6] as a solvent under the same catalytic conditions described in Table 1. Catalyst **4d** was recycled up to (see Supporting Information): (*i*) 10 consecutive runs for **7a**, with reaction times from 10 min to 10 h and with yields of 96−99% (accumulative TON 200); (*ii*) nine consecutive runs for **7b**, with reaction times from 15 min to 18 h and with yields of 96−99% (accumulative TON 176); (*iii*) six consecutive runs for **7c**, with reaction times from 30 min to 9 h and with yields of 95−99% (accumulative TON 118); (*iv*) nine consecutive runs for **7d**, with reaction times from 10 min to 9 h and with yields of 92−99% (TON 175); (*v*) 10 consecutive runs for **7e**, with reaction times from 5 min to 9 h and with yields of 94−99% (TON 195); and (*vi*) six consecutive runs for **7f**, with reaction times from 15 min to 10 h and with yields of 82−99% (TON 115). These data clearly reveal that the catalytic system suffered a gradual decrease of the activity after each recycling for all the substrates used (propargylic alcohols **7a−f**). Thus, in all cases, for the first cycles (see Supporting Information) less than 1 h was needed to achieve quantitative conversion, while more than 9 h for the last cycle was always required, probably due to both leaching during the workup and decomposition of the catalyst.

The catalytic activity of complex **4d** was then tested in the isomerization of propargylic alcohols which contain a C−H bond in the *β*-position with respect to the alcohol group (**9a,b**), which proceeds in a different way, giving rise to the selective formation of *α,β*-unsaturated methyl ketones (**10a,b**) as the result of a formal Rupe-type rearrangement of the alkynol (see Table 2).[29] A quantitative transformation is also achieved although (*i*) a higher temperature with respect to the aforementioned Meyer−Schuster rearrangement (130 vs 80 °C) and (*ii*) a longer reaction time were needed (see Table 1). The catalyst **4d** could be also recycled but remains active through a lower number of consecutive runs, i.e., for **9a** [first cycle, 3 h (96%); second cycle, 14.5 h (93%); third cycle, 48 h (46%)]; for **9b** [first cycle, 1.5 h (99%); second cycle, 3.5 h (99%); third cycle, 5 h (98%); fourth cycle, 20 h (97%)]. This catalytic transformation can also be applied successfully to a more elaborated substrate such as the hormonal steroid mestranol (**9c**, entry 3, Table 2). The corresponding enone **10c**, which is an important building block in the chemistry of steroids, has been obtained selectively in a pure form with excellent yield (99%). Unfortunately, the catalytic activity of **4d** with mestranol remained active for only one further cycle (quantitative transformation after 10 h) and without the formation of byproducts (GC or NMR spectra).

When internal propargylic alcohols such as PhC≡CC(OH)-Ph_2 or MeC≡CCH_2(OH) were used as substrates, no transformation was observed (polymerization is observed with

Table 2. Isomerization of Propargylic Alcohols 9a−c into *α,β*-Unsaturated Ketones 10a−c Catalyzed by Complex 4d in [BMIM][PF_6].[a]



Entry	Product		Time [hours]	GC Yield [%]	Isolated Yield [%]
1		**10a**	3	96	90
2		**10b**	1.5	99	91
3		**10c**	3	99	93

[a]Reactions were performed under a N_2 atmosphere at 130 °C, using 1 mmol of the corresponding alkynol in 1 g of [BMIM][PF_6] and with a catalyst loading of 5 mol % in Re.

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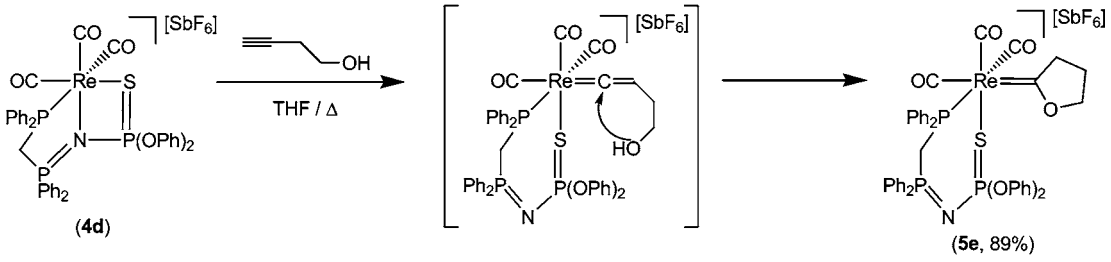
Scheme 4. Synthesis of the Cationic Tricarbonyl Re(I) Oxacyclic Carbene Complex 5e



the primary propargylic alcohol HC≡CCH$_2$OH). The absence of catalytic activity with internal alkynols is in accord with the proposed catalytic mechanism which seems to be based on the key intermediate hydroxyvinylidene complex [Re]$^+$=C=C(H)C(OH)R$_2$.[30] As is well-known, only terminal alkynols are able to undergo tautomerization to yield vinilydene-type species.[31] In order to assess the formation of the required intermediate rhenium(I) hydroxyvinylidene complex, the stoichiometric reaction of catalyst **4d** with various alkynols was carried out in [BMIM][PF$_6$]. Unfortunately, all attempts to isolate or characterize the reaction product have been unsuccessful. In contrast, when the reaction of complex **4d** with 3-butyn-1-ol (see Scheme 4) was performed in refluxing THF instead of the ionic liquid, the new Re-oxocyclocarbene complex [Re{=C(CH$_2$)$_3$O}(κ^2-*P,S*-Ph$_2$PCH$_2$P{=NP=S)(OPh)$_2$}Ph$_2$)(CO)$_3$][SbF$_6$] (**5e**) was selectively obtained. This carbene results from the well established intramolecular attack of the hydroxyl group on the α-carbon of the vinylidene intermediate complex (Scheme 4).[32] The rhenium(I)−oxacyclocarbene **5e** was characterized by multinuclear NMR (^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H}, see Experimental Section and Supporting Information). In particular, ^{1}H and ^{13}C{^{1}H} NMR spectra display the expected signals for the metalacycle fragment: (*i*) four proton resonances for the six protons of the five-membered ring appearing as multiplets at 4.56 ppm (2H), 3.09 and 2.70 (1H each), and 1.59 (2H) ppm and (*ii*) three carbon resonances at 20.07, 60.88, and 88.91 ppm, for the four carbon atoms of the five-membered ring along with a doublet of doublet signal at 305 (J_{CP} = 8.6 and 8.5 Hz) ppm, indicating the presence of the carbene Re=C bound.[32] In addition, the ^{31}P{^{1}H} spectrum displays the expected signals for a κ^2-*P,S* coordination of the iminophosphorane−phosphine ligand **1d** (see Experimental Section).

Moreover, the structure of cationic tricarbonyl−rhenium(I) oxacyclic carbene complex **5e** was unambiguously confirmed by means of a single-crystal X-ray diffraction study. An ORTEP-type view of the molecule is shown in Figure 6; selected bond distances and angles are listed in the caption. Again, the geometry around the metal is slightly distorted octahedral (see values in caption of Figure 6), the Re−C≡O, Re−P, and Re−S bond distances and interligand angles fitting well with those previously observed by us in complexes **5b** and **6a**, both containing the κ^2-*P,S* coordinated iminophosphorane−phosphine ligand **1d**. The Re=C bond distance (2.121(5) Å) is equal to that previously described for an analogous Re-cycloxycarbene complex (2.121(9) Å).[32] The isolation of **5e** is in accord with the formation of hydroxyvinylidene species as key intermediates in the ruthenium catalyzed rearrangement of propargylic alcohols into α,β-unsaturated carbonyl compounds.[27a] The absence of reaction with internal alkynols which are not able to form vinylidene species, and the fact that the catalytic reactions do not proceed without the presence of the catalyst **4d** in the ionic liquid at 80 °C, points to the classic mechanism based on the π-coordination of the propargylic alcohol and subsequent formation of vinylidene complex *via* a [1,2]-shift.[33,34]

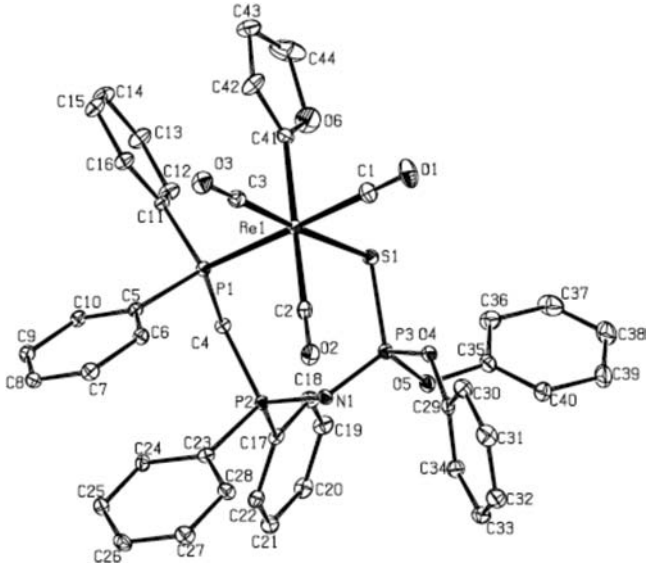


Figure 6. ORTEP-type view of the structure of the cation [Re{=C(CH$_2$)$_3$O}(κ^2-*P,S*-Ph$_2$PCH$_2$P{=NP(=S)(OPh)$_2$}Ph$_2$)(CO)$_3$]$^+$ of **5e** showing the crystallographic labeling scheme. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 20% probability level. Selected bond lengths (Å) and angles (deg): Re−P(1) = 2.461(1); Re−C(41) = 2.121(5); Re−S(1) = 2.574(1); Re−C(1) = 1.964(5); Re−C(2) = 1.979(5); Re−C(3) = 1.909(5); P(1)−C(4) = 1.847(4); C(4)−P(2) = 1.816(4); P(2)−N(1) = 1.592(3); N(1)−P(1) = 1.570(4); P(3)−S(1) = 1.991(2); P(1)−Re−S(1) = 88.34(3); P(1)−Re−C(41) = 89.3(12); S(1)−Re(1)−C(41) = 85.69(13); C(2)−Re−C(41) = 176.75(18); C(1)−Re−C(41) = 89.46(19); C(3)−Re−C(41) = 89.56(19).

CONCLUSION

In summary, in the present work we have described the high-yield synthesis of a series of new tricarbonyl rhenium(I) complexes containing the iminophosphorane−phosphine ligands Ph$_2$PCH$_2$P(=NR)Ph$_2$ (**1a−g**), which show a versatile coordination ability: (*a*) κ^2-*P,O*- in complexes [ReBr(κ^2-*P,O*-Ph$_2$PCH$_2$P{=NP(=O)(OR)$_2$}Ph$_2$)(CO)$_3$] (R = Et (**2a**), R = Ph (**2b**)), (*b*) κ^2-*P,S*- in complexes [ReBr(κ^2-*P,S*-Ph$_2$PCH$_2$P{=NP(=S)(OR)$_2$}Ph$_2$)(CO)$_3$] (R = Et (**2c**), Ph (**2d**)); (*c*) κ^2-*P,N*- in complexes [ReBr(κ^2-*P,N*-Ph$_2$PCH$_2$P{=NR}Ph$_2$)(CO)$_3$] (R = P(=O)(OEt)$_2$ (**3a**), P(=O)(OPh)$_2$ (**3b**), 4-C$_6$F$_4$CHO (**3e**), 4-C$_6$F$_4$CN (**3f**), 4-C$_6$F$_5$N (**3g**)), and (*d*) κ^3-*P,N,S*- in complexes [Re(κ^3-*P,N,S*-Ph$_2$PCH$_2$P{=NP(=S)-

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$(OR)_2\}Ph_2)(CO)_3][SbF_6]$ (R = Et (**4c**), R = Ph (**4d**)). Furthermore, the potential hemilabile properties of ligand **1d** have been proven in the reactivity of the cationic complex $[Re(\kappa^3\text{-}P,N,S\text{-}Ph_2PCH_2P\{=NP(=S)(OPh)_2\}Ph_2)(CO)_3][SbF_6]$ (**4d**), which reacts under very mild reaction conditions (*via* selective cleavage of the Re−N bond in the κ^3-*P,N,S* chelating ring) with the appropriate neutral (L) or anionic (Y^-) ligand to afford, respectively, the cationic derivatives $[Re(L)(\kappa^2\text{-}P,S\text{-}Ph_2PCH_2P\{=NP(=S)(OPh)_2\}Ph_2)(CO)_3][SbF_6]$ (L = Me_2C=O (**5a**), CH_3CN (**5b**), pyridine (**5c**), PPh_3 (**5d**)) and the neutral derivatives $[ReY(\kappa^2\text{-}P,S\text{-}Ph_2PCH_2P\{=NP(=S)(OPh)_2\}Ph_2)(CO)_3]$ (Y = Cl (**6a**), I (**6b**), N_3 (**6c**)), in excellent yields.

In addition, the cationic complex $[Re(\kappa^3\text{-}P,N,S\text{-}Ph_2PCH_2P\{=NP(=S)(OPh)_2\}Ph_2)(CO)_3][SbF_6]$ (**4d**) is a highly efficient catalyst for the isomerization of terminal propargylic alcohols into enals (Meyer−Schuster rearrangement) or enones (Rupe rearrangement) using the ionic liquid $[BMIM][PF_6]$ as nonconventional media. The isolation and X-ray characterization of the rhenium(I) oxacyclocarbene complex $[Re\{=C(CH_2)_3O\}(\kappa^2\text{-}P,S\text{-}Ph_2PCH_2P\{=NP(=S)(OPh)_2\}Ph_2)(CO)_3][SbF_6]$ (**5e**) obtained from the intramolecular attack of the hydroxyl group on the α-carbon of the vinylidne intermediate complex is also reported. The isolation of complex **5e** is in accord with the formation of hydroxyvinylidene species as key intermediates in ruthenium catalyzed rearrangement of propargylic alcohols into α,β-unsaturated carbonyl compounds.

EXPERIMENTAL SECTION

General Comments. The manipulations were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenck techniques. All reagents were obtained from commercial suppliers and used without further purification with the exception of compounds $Ph_2PCH_2P\{=NP(=X)(OR)_2\}Ph_2$ (X = O, R = Et (**1a**), Ph (**1b**);[6c] X = S, R = Et (**1c**), Ph (**1d**)[6d]), $Ph_2PCH_2P(=NR_F)Ph_2$ (R_F = 4-C_6F_4CHO (**1e**), 4-C_6F_4CN (**1f**), 4-C_6F_5N (**1g**)),[6b,13] and $[ReBr(CO)_5]$,[35] which were prepared by following methods reported in the literature. Propargylic alcohols **7a−f** and **9a−c** were obtained from commercially suppliers or synthesized by following the classical Midland's procedure.[36] Infrared spectra were recorded on a Perkin-Elmer 1720-XFT spectrometer. The C, H, and N analyses were carried out with a Perkin-Elmer 2400 microanalyzer. NMR spectra were recorded on a Bruker DPX300 instrument at 300 MHz (^{1}H), 121.5 MHz (^{31}P), or 75.4 MHz (^{13}C) using $SiMe_4$ or 85% H_3PO_4 as standards. DEPT experiments have been carried out for all the compounds reported in this paper. GC measurements were made on Hewlett−Packard HP6890 chromatograph equipped with an HP-INNOWAX cross-linked poly(ethyleneglycol) (30 m, 250 mm) or Supelco Beta-Dex 120 (30 m, 250 mm) column. GC/MS measurements were performed on Agilent 6890N equipment coupled to a 5973 mass detector (70 eV electron impact ionization) using a HP-1MS column.

Preparations. *$[ReBr(\kappa^2\text{-}P,X\text{-}Ph_2PCH_2P\{=NP(=X)(OR)_2\}Ph_2)(CO)_3]$ (X = O, R = Et (**2a**), Ph (**2b**); X = S, R = Et (**2c**), Ph (**2d**)] and $[ReBr(\kappa^2\text{-}P,N\text{-}Ph_2PCH_2P(=NR)Ph_2)(CO)_3]$ (R = P(=O)(OEt)$_2$ (**3a**), P(=O)(OPh)$_2$ (**3b**), 4-C_6F_4CHO (**3e**), 4-C_6F_4CN (**3f**), 4-C_6F_5N (**3g**)).* A solution of the Re(I) precursor $[ReBr(CO)_5]$ (0.203 g, 0.5 mmol) and the corresponding iminophosphorane−phosphine ligand **1a−g** (0.5 mmol) in 30 mL of THF was stirred at refluxing temperature for 8 h. The solution was then concentrated to *ca.* 2 mL, and hexane (30 mL) was added, yielding a white microcrystalline solid which was washed with diethyl ether (3 × 20 mL) and vacuum-dried. Starting from the *N*-phosphorylated ligands **1a**,**b**, in both cases, an inseparable mixture containing complexes **2a** and **3a** in a 3:2 ratio in 82% yield (0.363 g) for **1a** and an inseparable mixture containing complexes **2b** and **3b** in a 1:1 ratio in 92% yield (0.451 g) for **1b** was obtained, respectively. In contrast, starting from the aryl-fluorinated ligands $Ph_2PCH_2P(=NR_F)Ph_2$ (R_F = 4-C_6F_4CHO (**1e**), 4-C_6F_4CN (**1f**), 4-C_6F_5N (**1g**)) the neutral complexes **3e−g** were selectively obtained in 91% (0.421 g), 87% (0.401 g), and 93% (0.418 g) yields, respectively. For the *N*-thiophosphorylated ligands **1c**,**d**, the neutral complexes **2c**,**d** were selectively obtained in 94% (0.423 g) and 96% (0.479 g) yields, respectively. $^{31}P\{^1H\}$ NMR signals for **2a** in $(CD_3)_2S$=O: 0.59 (s, PPh_2), 7.45 (d, $^2J_{PP}$ = 41.6 Hz, P(=O)(OEt)$_2$), 8.90 (d, $^2J_{PP}$ = 41.6 Hz, Ph_2P=N). For **2b** $^{31}P\{^1H\}$ NMR (CD_2Cl_2): −4.18 (d, $^2J_{PP}$ = 45.8 Hz, P(=O)(OPh)$_2$), 0.93 (s, PPh_2), 9.64 (d, $^2J_{PP}$ = 45.8 Hz, Ph_2P=N). For **2c** $^{31}P\{^1H\}$ NMR (CD_2Cl_2): −5.12 (d, $^3J_{PP}$ = 6.0 Hz, PPh_2), 13.38 (d, $^2J_{PP}$ = 30.5 Hz, Ph_2P=N), 57.04 (dd, $^2J_{PP}$ = 30.5 Hz, $^3J_{PP}$ = 6.0 Hz, P(=S)(OEt)$_2$). For **2d** $^{31}P\{^1H\}$ NMR (CD_2Cl_2): −5.23 (d, $^3J_{PP}$ = 7.1 Hz, PPh_2), 14.37 (d, $^2J_{PP}$ = 27.8 Hz, Ph_2P=N), 48.95 (dd, $^2J_{PP}$ = 27.8 Hz, $^3J_{PP}$ = 7.1 Hz, P(=S)(OPh)$_2$). For **3a** $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 9.00 (dd, $^2J_{PP}$ = 14.4 Hz, $^3J_{PP}$ = 7.9 Hz, P(=O)(OEt)$_2$), 11.89 (dd, $^2J_{PP}$ = 32.7 Hz, $^3J_{PP}$ = 7.9 Hz, PPh_2), 54.82 (dd, $^2J_{PP}$ = 32.7 and 14.4 Hz, Ph_2P=N). For **3b** $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 0.36 (dd, $^2J_{PP}$ = 17.8 Hz, $^3J_{PP}$ = 8.3 Hz, P(=O)(OPh)$_2$), 10.81 (dd, $^2J_{PP}$ = 32.2 Hz, $^3J_{PP}$ = 8.3 Hz, PPh_2), 55.49 (dd, $^2J_{PP}$ = 32.2 and 17.8 Hz, Ph_2P=N). For **3e** $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 10.31 (d, $^2J_{PP}$ = 32.7 Hz, PPh_2), 49.21 (d, $^2J_{PP}$ = 32.7 Hz, Ph_2P=N). For **3f** $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 10.83 (d, $^2J_{PP}$ = 35.7 Hz, PPh_2), 52.07 (d, $^2J_{PP}$ = 35.7 Hz, Ph_2P=N). For **3g** $^{31}P\{^1H\}$ NMR ($(CD_3)_2S$=O): 10.80 (d, $^2J_{PP}$ = 35.7 Hz, PPh_2), 51.67 (d, $^2J_{PP}$ = 35.7 Hz, Ph_2P=N).

*$[Re(\kappa^1\text{-}O\text{-}Me_2C{=}O)(\kappa^2\text{-}P,S\text{-}Ph_2PCH_2P\{=NP(=S)(OPh)_2\}Ph_2)(CO)_3][SbF_6]$ (**5a**).* A solution of the cationic complex $[Re(\kappa^3\text{-}P,N,S\text{-}Ph_2PCH_2P\{=NP(=S)(OPh)_2\}Ph_2)(CO)_3][SbF_6]$ (**4d**) (0.576 g, 0.5 mmol) in acetone (30 mL) was stirred at room temperature for 1 min, and the solvate complex **5a** was immediately obtained in quantitative NMR yield (deuterated acetone was added to the sample to get the lock signal for the NMR measurement). Evaporation to dryness results in the regeneration of the precursor complex **4d**. $^{31}P\{^1H\}$ NMR ($(CD_3)_2C$=O): 10.80 (s, PPh_2), 15.45 (d, $^2J_{PP}$ = 30.7 Hz, Ph_2P=N), 43.83 (d, $^2J_{PP}$ = 30.7 Hz, P(=S)(OPh$_2$)).

*$[Re(\kappa^1\text{-}N\text{-}NCCH_3)(\kappa^2\text{-}P,S\text{-}Ph_2PCH_2P\{=NP(=S)(OPh)_2\}Ph_2)(CO)_3][SbF_6]$ (**5b**).* A solution of the cationic complex $[Re(\kappa^3\text{-}P,N,S\text{-}Ph_2PCH_2P\{=NP(=S)(OPh)_2\}Ph_2)(CO)_3][SbF_6]$ (**4d**) (0.576 g, 0.5 mmol) in acetonitrile (30 mL) was stirred at room temperature for 15 min and then evaporated to dryness. The resulting white oil was washed with diethyl ether (3 × 20 mL), affording a white solid which was vacuum-dried (97%, 0.580 g). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 4.02 (s, PPh_2), 15.45 (d, $^2J_{PP}$ = 31.7 Hz, Ph_2P=N), 44.91 (d, $^2J_{PP}$ = 31.7 Hz, P(=S)(OPh$_2$)).

*$[Re(L)(\kappa^2\text{-}P,S\text{-}Ph_2PCH_2P\{=NP(=S)(OPh)_2\}Ph_2)(CO)_3][SbF_6]$ (L = pyridine (**5c**), PPh_3 (**5d**)).* A solution of the cationic complex $[Re(\kappa^3\text{-}P,N,S\text{-}Ph_2PCH_2P\{=NP(=S)(OPh)_2\}Ph_2)(CO)_3][SbF_6]$ (**4d**) (0.576 g, 0.5 mmol) and the appropriate two electron ligand (5 mmol) in dichloromethane (30 mL) was stirred at room temperature for the indicated time. The solution was then concentrated to *ca.* 2 mL, and diethyl ether was added, yielding a yellow microcrystallyne solid which was washed with diethyl ether (3 × 20 mL) and vacuum-dried. (**5c**) Reaction time: 10 h. Yield 98% (0.604 g). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 5.72 (s, PPh_2), 14.79 (d, $^2J_{PP}$ = 31.7 Hz, Ph_2P=N), 43.10 (d, $^2J_{PP}$ = 31.7 Hz, P(=S)(OPh$_2$)). (**5d**) Reaction time: 2 h. Yield 92% (0.651 g). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): −10.22 (m, PPh_3), −1.13 (m, PPh_2), 16.23 (m, Ph_2P=N), 44.52 (m, P(=S)(OPh$_2$)).

*$[Re\{=C(CH_2)_3O\}(\kappa^2\text{-}P,S\text{-}Ph_2PCH_2P\{=NP(=S)(OPh)_2\}Ph_2)(CO)_3][SbF_6]$ (**5e**).* A solution of the cationic complex $[Re(\kappa^3\text{-}P,N,S\text{-}Ph_2PCH_2P\{=NP(=S)(OPh)_2\}Ph_2)(CO)_3][SbF_6]$ (**4d**) (0.576 g, 0.5 mmol) and but-3-yn-1-ol (0.038 mL, 0.5 mmol) in THF (30 mL) was stirred at refluxing temperature for 5 h. The solution was then concentrated to *ca.* 2 mL, and hexane was added, yielding a white microcrystallyne solid which was washed with diethyl ether (3 × 20 mL) and vacuum-dried. Yield 89% (0.545 g). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): −2.15 (s, PPh_2), 16.11 (d, $^2J_{PP}$ = 32.6 Hz, Ph_2P=N), 49.13 (d, $^2J_{PP}$ = 32.6 Hz, P(=S)(OPh$_2$)).

*$[ReY(\kappa^2\text{-}P,S\text{-}Ph_2PCH_2P\{=NP(=S)(OPh)_2\}Ph_2)(CO)_3]$ (Y = Cl (**6a**), I (**6b**), N_3 (**6c**)).* A solution of the cationic complex $[Re(\kappa^3\text{-}P,N,S\text{-}Ph_2PCH_2P\{=NP(=S)(OPh)_2\}Ph_2)(CO)_3][SbF_6]$ (**4d**) (0.576 g, 0.5 mmol) and the appropriate sodium salt NaX (5 mmol) in

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dichloromethane (30 mL) was stirred at room temperature for one hour. The suspension was filtered through Kieselghur and the resulting clear solution concentrated to *ca.* 2 mL. The addition of diethyl ether (40 mL) afforded a white microcrystalline solid which was washed with diethyl ether (3 × 20 mL) and vacuum-dried. (**6a**) Yield 95% (0.453 g). $^{31}P\{^1H\}$ NMR ($(CD_3)_2C{=}O$): −0.59 (d, $^3J_{PP}$ = 6.8 Hz, PPh_2), 13.84 (d, $^2J_{PP}$ = 25.0 Hz, $Ph_2P{=}N$), 47.62 (dd, $^2J_{PP}$ = 25.0 Hz, $^3J_{PP}$ = 6.8 Hz, $P(=S)(OPh_2)$). (**6b**) Yield 94% (0.491 g). $^{31}P\{^1H\}$ NMR ($(CD_3)_2C{=}O$): 11.08 (s, PPh_2), 15.87 (d, $^2J_{PP}$ = 31.5 Hz, $Ph_2P{=}N$), 44.17 (d, $^2J_{PP}$ = 31.5 Hz, $P(=S)(OPh_2)$). (**6c**) Yield 97% (0.465 g). $^{31}P\{^1H\}$ NMR ($(CD_3)_2C{=}O$): 3.39 (s, PPh_2), 14.91 (d, $^2J_{PP}$ = 25.5 Hz, $Ph_2P{=}N$), 45.32 (d, $^2J_{PP}$ = 25.5 Hz, $P(=S)(OPh_2)$).

General Procedure for the Catalytic Propargylic Isomerization in [BMIM][PF_6]. The rhenium catalyst **4d**, the ionic liquid [BMIM][PF_6] (1 g), and the corresponding alkynol (1 mmol) were introduced into a Schlenck tube undera nitrogen atmosphere. The mixture was then heated at 80 or 130 °C for the indicated time (the course of the reaction was monitored by regular sampling and analysis by GC). After completion of the reaction, the organic product was extracted with diethyl ether (3 × 5 mL). The organic crude reaction was purified by flash chromatography over silica gel using EtOAc/hexane (1:10) as an eluent. The identity of the resulting α,β-unsaturated carbonyl compounds was assessed by comparison of their ^1H and $^{13}C\{^1H\}$ NMR spectroscopic data with those reported in the literature and by their fragmentation in GC/MS.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Analytical and spectroscopic data for compounds **2a−d**, **3a−b**,**e−g**, **5b−e**, and **6a−c** have been provided. The recycling procedure for catalyst **4d** in the isomerization of propagylic alcohols **7a−f** using [BMIM][PF_6] as solvent is described. Crystallographic data for **3e**, **5b**, **5e**, and **6a** are also reported. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

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(12) We have previously reported the selective *S*-coordination of the *N*-thiophosphoryl-iminophosphoranyl fragment in Ru(II) centers, see ref 6d.

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(29) By monitoring the catalytic isomerization of propargylic alcohols **9** into enones **10** by GC/MS, the intermediate formation of the corresponding terminal 1,3-enynes $HC{\equiv}C{-}C(R'){=}CR_2$ was observed. Unfortunately, all attempts to prevent the subsequent hydration step were unsuccessful disabling the selective synthesis of the 1,3-enynes.

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