ORGANOMETALLICS

1,3-Dimethyl-4-(diphenylphosphino)imidazolium Triflate: A Functionalized Ionic Liquid with Ambivalent Coordination Capability

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S Supporting Information

ABSTRACT: Simply using 1-methylimidazole as the starting material, the functionalized ionic liquid 1,3-dimethyl-4-(diphenylphosphino)imidazolium triflate ([3]OTf) has been prepared, from which the corresponding 4-phosphino-substituted N-heterocyclic carbene 4 was generated. The coordination capability of 3 and 4 toward a variety of transition-metal centers has been studied, as well as their electron-donor character through an evaluation of the TEP parameter. 3 behaves as a cationic phosphine ligand, whereas 4 shows a strong preference to coordinate to transition metals through the carbene carbon atom, leading to the obtention of mononuclear complexes with a free phosphine arm which act



as metalloligands, allowing for the modular formation of homo- and heterodinuclear transition-metal complexes.

INTRODUCTION

1,3-Dialkylimidazolium salts are currently receiving a great deal of attention, owing to their use as ionic liquids for novel media in organic synthesis and catalysis¹ and as precursors of Nheterocyclic carbenes (NHCs).² Recently, imidazolium salts containing functional groups have been used for task-specific applications,³ such as separation of CO₂ from gas streams,⁴ supports for organic synthesis,⁵ extraction of metal ions, construction of nanostructures,⁷ and ion conductive materials.⁸ Particularly, phosphino-functionalized imidazolium salts, most of them containing the phosphino group connected to a nitrogen atom of the imidazolium cycle through a carbon spacer, have been extensively employed in the formation of chelating or pincer NHC-phosphine ligands⁹ and as ionophilic phosphines for ionic-liquid biphasic catalysis.¹⁰ In recent pioneering works, the groups of Bertrand¹¹ and Gates¹² have described the synthesis of 4-phosphino-substituted 1,3-diarylimidazol-2-ylidenes and proved their suitability for the synthesis of several dimetallic transition-metal complexes.¹³ Subsequently our group managed to isolate 4,5-diphosphinosubstituted imidazolium salts and use them for generating mixed diphosphine-NHC ligands.^{14,15} In related studies, 4phosphorylimidazolium and 4,5-bis(phosphoryl)imidazolium salts have also been prepared, some of them being remarkable examples of room-temperature ionic liquids, as well as their corresponding NHC-transition-metal complexes.¹⁶

In this paper we describe the synthesis of the functionalized ionic liquid 1,3-dimethyl-4-(diphenylphosphino)imidazolium triflate ([3]OTf; Figure 1), which contains one of the simplest imidazolium scaffolds, and the study of its properties and coordination capabilities together with those of the corresponding NHC derivative. A comparison has been made with its



Figure 1. Parent 1,3-dimethylimidazolium triflate ([1]OTf) and its diphenylphosphino-functionalized derivatives [2]OTf and [3]OTf (this work). OTf = $CF_3SO_3^-$.

isomer 1,3-dimethyl-2-(diphenylphosphino)imidazolium triflate ([2]OTf) as well as with the parent unsubstituted imidazolium salt ([1]OTf).

RESULTS AND DISCUSSION

As summarized in Scheme 1, the salt 1,3-dimethyl-4-(diphenylphosphino)imidazolium triflate ([3]OTf) has been prepared by using a one-pot procedure starting from 1methylimidazole (A). This is first reacted with BuLi and ClPPh₂ to afford the phosphine **B**, which in a following step is treated with MeOTf to give the 2-phosphinoimidazolium salt [2]-OTf,¹⁷ resulting from chemoselective methylation at the iminic nitrogen atom. Isomerization of **2** to **3** is carried out by treatment with LiHMDS and quenching with water. [3]OTf was obtained as colorless crystals in high yield. Undoubtedly, deprotonation of **2** should afford initially the corresponding

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Scheme 1. Formation of the Imidazolium Cation 3 and Its Corresponding NHC 4



mesoionic carbene C¹⁸, which is then transformed into carbene **4** after migration of the phosphino substituent.

Compound 4 was detected by ³¹P{¹H} NMR during the reaction course but could not be isolated, owing to its exceeding propensity for protonation. Nevertheless, carbene 4 could be characterized by ¹H and ¹³C{¹H} NMR spectroscopy by reaction of a freshly prepared solution of pure crystals of [3] OTf in C_6D_6 with LiHMDS in the NMR tube. A high-field resonance at 203.7 ppm typical of a carbene carbon atom together with two singlets at 3.37 and 3.70 ppm for the hydrogen atoms of the two inequivalent methyl substituents are the most characteristic signals of this new phosphinofunctionalized carbene. Meanwhile, the imidazolium salt [3]OTf shown a characteristic high-field singlet in the proton spectrum (9.20 ppm) for the C2-H hydrogen atom. An X-ray crystal structure analysis of [3]OTf (Figure 2) was carried out, showing typical bond lengths and angles for imidazolium cations.^{2f} Short C2-H...O contacts were found within the crystal ranging from 2.29 to 2.71 Å, proving the existence of hydrogen bonds with the triflate anion, which should be



Figure 2. View of the structure of [3]OTf, shown with 50% thermal ellipsoids. Hydrogen atoms (except C2–H and C5–H) are omitted for clarity. Selected bond distances (Å) and angles (deg): N1–C2 = 1.327(5), C2–N3 = 1.333(5), N3–C4 = 1.387(5), C4–C5 = 1.364(5), C5–N1 = 1.375(5), C4–P1 = 1.819(4), N1–C1 = 1.461(5), N3–C3 = 1.471(5); N1–C2–N3 = 108.2(4), C2–N3–C4 = 109.5(3), N3–C4–C5 = 105.6(3), C4–C5–N1 = 107.7 (4), C5–N1–C2 = 109.0(3), N3–C4–P1 = 122.0(3), C5–C4–P1 = 131.8(3).

maintained to some extent in solution in view of the relatively high chemical shift of the C2–H proton in the ¹H NMR spectrum.

The parent imidazolium salt MeMeIm⁺OTf⁻ ([1]OTf) is reported to have a melting point of 39 °C.¹⁹ The inclusion of a diphenylphophino substituent on carbon atom C2 (compound [2]OTf) considerably increases the melting point value up to 104 °C, whereas changing the position of this group from C2 to C4 (compound [3]OTf) leads to an appreciably lower melting point of 86 °C: that is, below the 100 °C threshold which is generally admitted for considering a salt to be an ionic liquid.¹

Compound [3]OTf behaves as an imidazolium-functionalized phosphine ligand forming a variety of complexes with transition metals, as summarized in Scheme 2. Thus, the





treatment of [3]OTf with $[AuCl(SMe_2)]$ and $[RhCl(COD)]_2$ at room temperature readily afforded complexes **5** and **6**, respectively, whereas reaction of [3]OTf with the carbonyl compound $[Mo(CO)_6]$ requires several hours of refluxing in toluene to achieve substitution of a carbon monoxide molecule to give complex 7. All three compounds were fully characterized by spectroscopic methods (see the Experimental Section). The ³¹P{¹H} NMR spectra showed typical low-field shifts of the phosphorus signal with respect to that of the free ligand, whereas the ¹H and ¹³C{¹H} NMR spectra are very similar to those of **3**. Coordination of two phosphine ligands to

the same metal was also easily accomplished by reacting AgOTf with 2 equiv of 3, giving the tricationic complex 8. This example illustrates the possibility of forming highly charged transition-metal Lewis acids using the cationic phosphine 3 as a ligand for future catalytic applications.²⁰ The ${}^{31}P{}^{1}H$ NMR of 8 at room temperature afforded a broad singlet at -13.0 ppm, owing to dissociation of the phosphine ligand, which is split up into two doublets when measuring the spectrum at low temperature due to the coupling of the phosphorus atoms with 107 Ag and 109 Ag isotopes $(^{1}J(P,Ag) = 488$ and 562 Hz, respectively). The presence of two phosphine ligands per silver atom within the complex was confirmed by an ¹⁰⁹Ag{³¹P} INEPT NMR measurement²¹ carried out at low temperature, giving a triplet signal at 754.2 ppm (one-up/one-down appearance typical of the A part of an AX₂ spin system), due to the coupling of ¹⁰⁹Ag with the two equivalent phosphorus atoms.

Looking at the ν (CO) frequencies of the carbonyl ligands in the IR spectrum of complex 7 (2078 (m), 1952 (vs) cm^{-1}), we come to the conclusion that the phosphine 3 is moderately less donating than a typical triarylphosphine such as triphenylphosphine (bands at 2073 and 1945 cm⁻¹ for the complex $[Mo(CO)_5(PPh_3)])$,²² which is due to the electron-withdrawing character of the imidazolium substituent at 3. The same conclusion is gained by analyzing the ν (CO) bands of the rhodium(I) complex $[RhCl(CO)_2(3)]$ (9), which is prepared by bubbling carbon monoxide into a dichloromethane solution of 6 (Scheme 2). The average value of these bands in 9 is 2065 cm^{-1} , which accounts for a TEP (Tolman electronic parameter)²³ of 2072 cm^{-1} for the cationic phosphine 3. This TEP value is appreciably higher than that of PPh_3 (2063 cm⁻¹) calculated from the complex $[RhCl(CO)_2(PPh_3)]^{24}$ and is similar to those found in phosphite ligands.^{20a} Note that the TEP parameter is commonly used to evaluate the electrondonor character of different ligands, in such a way that the lower the TEP value, the stronger the donor ability of the ligand.²³ The imidazolium cation 2, bearing the phosphino substituent at carbon atom C2, shows a TEP value of 2082 cm^{-1} ²⁵ being clearly more weakly electron donating than 3, which emphasizes the strong influence of placing the phosphino group on different carbon atoms of the imidazolium cycle. In fact, 2 has also been considered as a NHC-stabilized phosphenium adduct,²⁶ whereas 3 has features typical of phosphine ligands.

Complex 9 was very unstable in solution, precluding NMR spectroscopic characterization, as it spontaneously loses CO and is transformed into the monocarbonyl complex 10 (Scheme 2) containing two phosphine ligands 3 coordinated to rhodium. Complex 10 features a sole ν (CO) band in the IR spectrum at 1995 cm⁻¹, whereas the ³¹P{¹H} NMR spectrum shown a doublet at 16 ppm $({}^{1}J(Rh,P) = 129.5 \text{ Hz})$ for the two equivalent, mutually trans phosphine ligands. The signals of the proton and carbon NMR spectra are very similar to those found in the free ligand 3. The structure of 10 in the solid state was definitively stablished by single-crystal X-ray diffraction analysis. A view of the structure is shown in Figure 3 together with selected bond distances and angles, from which it can be appreciated that the imidazolium cycle features structural parameters very similar to those found in the free imidazolium salt 3 (Figure 2).

Once the coordination capability of **3** was assessed, we proceeded to study that of its deprotonated form. The 4-phosphino-functionalized N-heterocyclic carbene **4** contains



Figure 3. Molecular structure of the cationic complex **10**, shown with 50% thermal ellipsoids. Hydrogen atoms (except C2–H, C5–H, C12–H, and C15–H) are omitted for clarity. Selected bond distances (Å) and angles (deg): N1–C2 = 1.329(4), C2–N3 = 1.322(4), N3–C4 = 1.396(4), C4–C5 = 1.358(5), C5–N1 = 1.373(4), C4–P1 = 1.804(3), N1–C1 = 1.462(4), N3–C3 = 1.460(4), N11–C12 = 1.315(5), C12–N13 = 1.326(4), Rh1–P1 = 2.3029(8), Rh1–P2 = 2.3142(8); N1–C2–N3 = 109.1(3), C2–N3–C4 = 108.9(3), N3–C4–C5 = 105.7(3), C4–C5–N1 = 108.0(3), C5–N1–C2 = 108.4(3), N3–C4–P1 = 124.5(2), C5–C4–P1 = 129.5(3).

two donor atoms prone to coordination to a metal center: the carbene carbon atom and the phosphorus atom.

We have carried out reactions of 4 with different metal complexes, proving that the first choice for coordination was always through the carbone carbon atom, owing to its more strongly electron donating character (Scheme 3). In fact, the substitution reactions proceed under conditions milder than those in the case of the imidazolium precursor **3**. Thus, reaction of 4 (which was prepared in situ by reaction of [3]OTf with KOH) with $[Mo(CO)_6]$ took place at room temperature to afford the neutral pentacarbonyl NHC complex 11. Formation of the tetracarbonyl dicarbene complex 12 was also feasible by treatment of $[Mo(CO)_6]$ with 2 equiv of 4 in toluene, but in this case heating of the reaction mixture at 90 °C for 45 min is needed. In both new molybdenum carbene complexes the uncoordinated phosphorus atom appears as a singlet around -33 ppm in the ${}^{31}P{}^{1}H$ NMR spectrum, which is almost identical with that for free NHC 4. The ¹³C{¹H} NMR spectra of 11 and 12 show as the most noticeable signal singlets at 192.3 and 199.9 ppm, respectively, for the carbene carbon atoms.

When carbene 4 was reacted with 1/2 equiv of [RhCl-(COD)]₂, coordination of the ligand also occurred through the carbene carbon atom, producing complex 13, which shows a singlet in the ${}^{31}P{}^{1}H$ NMR spectrum around -33 ppm characteristic of the uncoordinated phosphorus atom. In contrast to what was found in the plethora of known stable carbene complexes of formula [RhCl(NHC)(COD)], compound 13 was highly unstable in solution, most probably due to the occurrence of an intermolecular nucleophilic attack of the free diphenylphosphino group to coordinated cyclooctadiene,² affording a highly insoluble material which so far remains uncharacterized.²⁸ This result anticipates a differential chemical behavior of these new phosphino-functionalized NHC complexes with respect to more conventional NHCs. If a freshly prepared solution of 13 is immediately treated with CO, the corresponding dicarbonyl complex 14 is quickly formed (Scheme 3), allowing for recording the IR spectrum before decomposition occurs. The average $\nu(CO)$ frequency was found to be 2044 cm^{-1} , which accounts for a TEP value of 2055



Scheme 3. Modular Formation of Mono- and Dimetallic Complexes Containing the Mixed NHC-Phosphine Ligand 4

cm⁻¹: that is, very similar to that of the nonfunctionalized parent carbene $ImNMe_2$ (2054 cm⁻¹)²⁹ and naturally appreciably lower than that of phosphine 3 (2072 cm⁻¹, see above), showing its stronger donor character.

Complex 11 can act as a metallophosphine, allowing the modular formation of dimetallic complexes. Thus, the reaction of 11 with 1 equiv of $[Mo(CO)_6]$ in refluxing toluene afforded the homodimetallic complex 15. Both carbon and phosphorus donor atoms are clearly identified in the ¹³C{¹H} NMR (197.3 ppm) and ${}^{31}P{}^{1}H$ NMR (16.7 ppm) spectra, while the IR spectrum in CH₂Cl₂ shows differentiated bands for the two inequivalent molybdenum pentacarbonyl fragments, those corresponding to the carbene complex (2064 and 1931 cm⁻¹) having substantially lower frequencies in comparison to those of the phosphine complex (2075 and 1948 cm^{-1}), clearly reflecting the stronger electron-donor character of the carbene carbon atom with respect to the phosphine group. Complex 15 can alternatively be prepared by reaction of 7 with $[Mo(CO)_6]$ in the presence of KOH as deprotonating agent. The crystal structure of 15 was determined by X-ray diffraction analysis. A view of the structure is presented in Figure 4, showing the new 4-diphenylphosphino-NHC 4 bridging two $[Mo(CO)_5]$ moieties. The bond distances and angles within the imidazole cycle are in the expected range for NHCs, which means slightly longer C2-N bond lengths and a closer N1-C2–N3 angle than in the imidazolium salt $3.^{21}$ The C–O bond length of the carbonyl ligand located in a trans position with



Figure 4. Molecular structure of 15, shown with 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): N1-C2 = 1.364(2), C2-N3 = 1.368(2), N3-C4 = 1.400(2), C4-C5 = 1.347(2), C5-N1 = 1.375(2), C4-P1 = 1.8144(17), N1-C1 = 1.462(2), N3-C3 = 1.457(2), M01-C2 = 2.2635(16), M02-P1 = 2.5353(5); N1-C2-N3 = 102.97(13), C2-N3-C4 = 111.90(14), N3-C4-C5 = 105.53(14), C4-C5-N1 = 107.59 (14), C5-N1-C2 = 112.01(14), N3-C4-P1 = 126.20(13), C5-C4-P1 = 127.39(14).

respect to the carbon atom C2 (1.153(2) Å) is slightly higher than that of the carbonyl ligand placed in a trans position with respect to the phosphorus atom P1 (1.145(2) Å), additionally reflecting the stronger electron-donor character of the carbene moiety.

Naturally, the formation of heterodimetallic complexes was also possible by using the above procedure. As an example, complex 11 was treated with 1/2 equiv of $[RuCl_2(p-cym)]_2$ in CH₂Cl₂ at room temperature, readily affording complex 16 (Scheme 3), which was fully spectroscopically characterized (see the Experimental Section for details).

Aiming to obtain TEP values of 4 when it is simultaneously coordinated to two rhodium(I) centers, we prepared the dimetallic complex 17 by reacting 3 with 1 equiv of [RhCl(COD)]₂ using LiHMDS as proton abstractor (obviously 17 can also be prepared in a similar way by starting from isolated 6). Among the spectroscopic data of 17, it is worth noting the presence of a typical low-field doublet (189.7 ppm, ${}^{1}J(Rh,C) = 51 \text{ Hz})$ for the carbon carbon atom in the ${}^{13}C{}^{1}H{}$ NMR spectrum, together with a doublet at 9.14 ppm $({}^{1}J(Rh,P)$ = 151 Hz) for the phosphino group in the ${}^{31}P{}^{1}H{}$ NMR spectrum. The bubbling of CO into a dichloromethane solution of 17 readily produces complex 18, which showed two $\nu(CO)$ bands in the IR spectrum for each $[RhCl(CO)_2]$ fragment. The average values of these bands were 2059 and 2044 cm⁻¹, which account for TEP values of 2067 and 2055 cm⁻¹ for the phosphine and carbene moieties of 4, respectively. Note that the TEP value of the carbene moiety remains unchanged with respect to the mononuclear complex 14 containing uncoordinated phosphorus, whereas the TEP value of the phosphine moiety slightly decreases with respect to that of complex 9 (2072 cm^{-1}) , which is logical because the neutral phosphine 4 is more electron donating than the cationic phosphine 3.

We have found a one-pot experimental procedure to synthesize the functionalized ionic liquid 1,3-dimethyl-4-(diphenylphosphino)imidazolium triflate ([3]OTf; mp 86 °C) and subsequently generate the corresponding 4-phosphino-substituted N-heterocyclic carbene 4, simply starting from the easily available 1-methylimidazole. The coordination capability of 3 and 4 toward a variety of transition-metal centers has been studied, as well as their electron-donor character through the evaluation of the TEP parameter from dicarbonyl Rh(I) derivatives. Several mononuclear complexes of Au(I), Ag(I), Mo(0), and Rh(I) containing 3 as a cationic phosphine ligand that features electron-donating ability similar to that of phosphite ligands have been prepared. 4 shows a strong preference to coordinate to transition metals through the carbene carbon atom, leading to the obtention of mononuclear complexes with a free phosphine moiety which act as metalloligands, allowing for the modular formation of homo- and heterodinuclear transition-metal complexes.

EXPERIMENTAL SECTION

General Considerations. All reactions and manipulations were performed under an atmosphere of dry nitrogen by standard Schlenk techniques. Solvents were distilled over appropriate drying agents under dry nitrogen before use. The IR spectra were measured with PerkinElmer Spectrum 100 and Paragon 1000 spectrophotometers. The C, H, and N analyses were performed on a PerkinElmer 240B elemental analyzer. NMR spectra were recorded on Bruker 300 and 400 MHz spectrometers. Coupling constants *J* are given in Hz. Chemical shifts of the NMR spectra were referenced to internal SiMe₄ (¹H and ¹³C) or external H₃PO₄ (³¹P). All reagents were obtained commercially and used without further purification.

Compound [2]OTf was prepared as described elsewhere,¹⁷ and its melting point was measured: 104 °C.

Compound [3]OTf. To a solution of 1-methylimidazole (97 μ L, d = 1.03 g/mL, 1.22 mmol) in THF (5 mL) at 193 K was added a hexane solution of nBuLi (761 µL, 1.6 M, 1.22 mmol) and the resulting mixture stirred for 1 h. Then, 1 equiv of ClPPh₂ (223 μ L, d = 1.229 g/mL, 98%, 1.22 mmol) was added to the solution. The mixture was warmed slowly to room temperature. The solvent was evaporated to dryness and the residue extracted with CH₂Cl₂ (5 mL) and filtered. Addition of methyl triflate (136 μ L, d = 1.496 g/mL, 98%, 1.22 mmol) to the solution and stirring for 30 min caused the formation of compound [2]OTf, as detected by ³¹P NMR spectroscopy. The solvent was evaporated to dryness and the residue dissolved in THF. Then LiN(SiMe₃)₂ (1.22 mL of a 1 M hexane solution, 1.22 mmol) was added to the solution and the mixture stirred for 30 min. The solvent was eliminated under vacuum, and the residue was successively washed with hexane $(2 \times 5 \text{ mL})$, dissolved in CH₂Cl₂ (10 mL), and treated with water (10 mL). The mixture was stirred for 1 h, and then the organic phase was filtered over diatomaceous earth. The solvent was evaporated to dryness and the resulting residue washed with hexane $(3 \times 10 \text{ mL})$ to obtain a white solid corresponding to [3]OTf, which was filtered and dried under vacuum. Colorless crystals suitable for X-ray analysis were obtained by slow diffusion of hexane into a solution of the compound in THF. Yield: 360 mg (70%). Mp: 86 °C. Anal. Calcd for C₁₈H₁₈N₂F₃O₃PS: C, 50.23; H, 4.22; N, 6.51. Found: C, 50.74; H, 4.31; N, 6.00. ¹H NMR (300 MHz, CD₂Cl₂, 25 °C): δ 9.20 (s, 1 H, N₂CH), 7.47–7.36 (m, 10 H, Ph), 6.52 (s, 1 H, =CH), 3.83 (s, 3 H, NMe), 3.71 (s, 3 H, NMe). ¹³C{¹H} NMR (75.46 MHz, CD_2Cl_2 , 25 °C): δ 141.3 (s, C2), 135.6 (d, ¹J(C,P) = 21.6 Hz, C4), 134.3–128.8 (Ph), 129.0 (d, ${}^{2}J(C,P) = 6.8$ Hz, C5), 36,9 (s, NMe), 35.5 (d, ${}^{3}J(C,P) = 9.6$ Hz, NMe). ${}^{31}P{}^{1}H{}$ NMR (121.48 MHz, CD_2Cl_2 , 25 °C): δ -34.2 (s, PPh₂). MS (FAB): m/z 281.2 [M - $CF_3SO_3]^+$.

Generation of Carbene 4. A solution of the salt [3]OTf in C_6D_6 was treated with 1 equiv of LiN(SiMe₃)₂ (1 M hexane solution) in an

NMR tube. After a few minutes, carbene 4 was formed quantitatively. ¹H NMR (400 MHz, $C_6D_{6^0}$ 25 °C): δ 7.37–7.29 (m, 5 H, Ph), 7.16– 7.15 (m, 5 H, Ph), 6.01 (s, 1 H, ==CH), 3.72 (s, 3 H, NMe), 3.39 (s, 3 H, NMe). ¹³C{¹H} NMR (100.61 MHz, $C_6D_{6^0}$ 25 °C): δ 204.1 (s, C2), 133.7–128.9 (Ph), 127.4 (s, C5), 36,5 (s, NMe), 36.0 (d, ³*J*(C,P) = 8.7 Hz, NMe). ³¹P{¹H} NMR (162.14 MHz, $C_6D_{6^0}$ 25 °C): δ –34.4 (s, PPh₂).

Compound [5]OTf. To a solution of [3]OTf (30 mg, 0.07 mmol) in CH₂Cl₂ (6 mL) was added 1 equiv of [AuCl(SMe₂)] (20.5 mg, 0.07 mmol) and the resulting mixture stirred for 15 min. The solution was filtered, and then the solvent was evaporated to dryness to obtain a white solid which was washed with hexane (2 × 10 mL). Colorless crystals of the compound were obtained from THF/hexane. Yield: 31 mg (67%). Anal. Calcd for C₁₈H₁₈N₂AuClF₃O₃PS.THF: C, 35.96; H, 3.57; N, 3.81. Found: C, 35.93; H, 3.49; N, 3.79. ¹H NMR (300 MHz, CD₂Cl₂, 25 °C): δ 9.32 (s, 1 H, N₂CH), 7.78–7.60 (m, 10 H, Ph), 6.83 (s, 1 H, =CH), 3.90 (s, 3 H, NMe), 3.85 (s, 3 H, NMe). ¹³C{¹H} NMR (75.46 MHz, CD₂Cl₂, 25 °C): δ 143.8 (s, C2), 134.9– 130.7 (Ph), 132.5 (d, ²J(C,P) = 12.5 Hz, CS), 125.8 (d, ¹J(C,P) = 71.3 Hz, C4), 123.9 (d, ¹J(C,P) = 66.7 Hz, C_{ipso} Ph), 37,4 (s, NMe), 36.8 (d, ³J(C,P) = 4.5 Hz, NMe). ³¹P{¹H} NMR (121.48 MHz, CD₂Cl₂, 25 °C): δ 10.1 (s, PPh₂). MS (FAB): *m/z* 513.0 [*M* – *CF*₃SO₃]⁺.

Compound [6]OTf. To a solution of [3]OTf (30 mg, 0.07 mmol) in CH₂Cl₂ (5 mL) was added 1/2 equiv of [RhCl(COD)]₂ (17 mg, 0.035 mmol) and the resulting mixture stirred for 15 min. The solution was then filtered and the solvent evaporated to dryness to obtain an orange solid, which was washed with hexane $(2 \times 10 \text{ mL})$. Yield: 41 mg (87%). Anal. Calcd for C₂₆H₃₀N₂ClF₃O₃PRhS: C, 46.13; H, 4.11; N, 3.81. Found: C, 46.59; H, 4.14; N, 4.13. ¹H NMR (300 MHz, CD₂Cl₂, 25 °C): δ 9.21 (s, 1 H, N₂CH), 7.61–7.49 (m, 10 H, Ph), 6.79 (s, 1 H, =CH), 5.64 (s, 2H, CH COD), 4.54 (s, 3 H, NMe), 3.82 (s, 3 H, NMe), 3.39 (s, 2H, CH COD), 2.39 (s, 4H, CH₂ COD), 2.18-2.01 (m, 4H, CH₂ COD). ¹³C{¹H} NMR (75.46 MHz, CD₂Cl₂, 25 °C): δ 142.0 (s, C2), 134.3-129.8 (Ph), 130.3 (s, C5), 128.4 (d, ${}^{1}J(C,P) = 46.0 \text{ Hz}, C4), 108.5 \text{ (m, CH COD)}, 73.1 \text{ (d, } {}^{1}J(C,Rh) =$ 12.8 Hz, CH COD), 38,5 (s, NMe), 37.0 (s, NMe), 33.4 (s, CH₂) COD), 29.3 (s, CH₂ COD). ${}^{31}P{}^{1}H{}$ NMR (121.48 MHz, CD₂Cl₂, 25 °C): δ 13.1 (d, $^{1}J(Rh, P) = 153.9$ Hz, PPh₂).

Compound [7]OTf. To a solution of [3]OTf (0.1 g, 0.23 mmol) in toluene (10 mL) was added 1 equiv of $[Mo(CO)_6]$ (61 mg, 0.23 mmol). The mixture was heated at 108 °C for 6 h. The solvent was then evaporated to dryness to form a white solid, which was washed with hexane (2 × 10 mL). Yield: 58 mg (37%). Anal. Calcd for C₂₃H₁₈N₂F₃MoO₈PS: C, 41.46; H, 2.72; N, 4.20. Found: C, 42.09; H, 2.43; N, 4.11. ¹H NMR (400 MHz, CD₂Cl₂, 25 °C): δ 9.34 (s, 1 H, N₂CH), 7.59 (br, 5 H, Ph), 7.57 (s, 5 H, Ph), 7.28 (s, 1 H, ==CH), 4.00 (s, 3 H, NMe), 3.50 (s, 3 H, NMe). ¹³C{¹H} NMR (100.61 MHz, CD₂Cl₂, 25 °C): δ 209.0 (d, ²*J*(C,P) = 25.5 Hz, CO *trans*), 205.3 (d, ²*J*(C,P) = 8.6 Hz, CO *cis*), 143.8 (s, C2), 132.8–130.3 (Ph), 37.4 (s, NMe), 37.2 (s, NMe). ³¹P{¹H} NMR (121.48 MHz, CD₂Cl₂, 25 °C): δ 21.9 (s, PPh₂). IR (CH₂Cl₂): ν (CO) 2078 (m), 1952 (vs) cm⁻¹. MS (FAB): *m*/z 519.0 [*M* - *CF*₃SO₃]⁺.

Compound [8](OTf)₃**.** To a solution of [3]OTf (0.1 g, 0.23 mmol) in CH₂Cl₂ (5 mL) was added 1/2 equiv of AgOTf (30 mg, 0.12 mmol) and the resulting mixture stirred for 24 h. The solution was filtered and the solvent evaporated to dryness, giving a white residue, which was washed with hexane $(2 \times 10 \text{ mL})$ to afford a white solid. Yield: 105 mg (76%). ¹H NMR (400 MHz, CD₂Cl₂, 25 °C): δ 9.07 (s, 2 H, N₂CH), 7.64–7.49 (m, 20 H, Ph), 6.69 (s, 2 H, =CH), 3.82 (s, 6 H, NMe), 3.71 (s, 3 H, NMe). ¹³C{¹H} NMR (75.46 MHz, CD₂Cl₂, 25 °C): δ 142.5 (s, C2), 134.6 (d, ²J(C,P) = 17.8 Hz, o-Ph), 133.3 (s, *p*-Ph), 131.1 (d, ${}^{2}J(C,P) = 7.1$ Hz, C5), 130.6 (d, ${}^{3}J(C,P) = 10.5$ Hz, *m*-Ph), 125.5 (d, ${}^{1}J(C,P) = 37.3$ Hz, C4), 37,0 (s, NMe), 36.5 (s, NMe). ³¹P{¹H} NMR (121.48 MHz, CD₂Cl₂, 25 °C): δ -13.0 (br, PPh₂), ${}^{31}P{}^{1}H$ NMR (121.48 MHz, CD₂Cl₂, - 80 °C): δ -13.0 (d, ${}^{1}J({}^{109}Ag,P) = 562$ Hz; d ${}^{1}J({}^{107}Ag,P) = 488$ Hz, PPh₂). ${}^{109}Ag\{{}^{31}P\}$ INEPT NMR (CD₂Cl₂, -80 °C): δ 754.2 (t, ¹*J*(¹⁰⁹Ag,P) = 558 Hz). MS (FAB): m/z 669.0 $[M - 3CF_3SO_3]^+$.

Compounds [9]OTf and [10](OTf)2. Carbon monoxide was bubbled through a solution of [6]OTf (60 mg, 0.083 mmol) in CH₂Cl₂ (5 mL) for 5 min. Immediate formation of the dicarbonyl compound [9]OTf was evidenced by the $\nu(CO)$ bands in the IR spectrum of the solution: 2106 (s), 2023 (vs) cm⁻¹. This spontaneously evolves to the monocarbonyl derivative [10](OTf)₂ on standing in solution. Orange crystals of [10](OTf)₂ suitable for Xray crystallography were obtained by slow diffusion of hexane into a solution of the compound in CH₂Cl₂. Yield: 25 mg (58%). Anal. Calcd for C₃₇H₃₆N₄ClF₆O₇P₂RhS₂: C, 43.27; H, 3.53; N, 5.45. Found: C, 43.53; H, 3.14; N, 5.30. ¹H NMR (300 MHz, CD₂Cl₂, 25 °C): δ 9.22 (s, 2 H, N₂CH), 7.81–7.74 (m, 10 H, Ph), 7.63–7.57 (m, 10 H, Ph), 6.81 (s, 2 H, =CH), 3.91 (s, 6 H, NMe), 3.86 (s, 6 H, NMe). ¹³C{¹H} NMR (75.46 MHz, CD₂Cl₂, 25 °C): δ 185.7 (s, CO), 142.6 (s, C2), 136.7–130.3 (Ph), 131.1 (s, C5), 127.8 (d, ${}^{1}J(C,P) = 50.6$ Hz, C4), 37,6 (s, NMe), 37.2 (s, NMe). ${}^{31}P{}^{1}H{}$ NMR (121.48 MHz, CD_2Cl_2 , 25 °C): δ 16.0 (d, ${}^{1}J(Rh,P) = 129.5$ Hz, PPh_2).). IR $(CH_2Cl_2): \nu(CO)$ 1995 (vs) cm⁻¹.

Compound 11. To a solution of [3]OTf (0.1 g, 0.23 mmol) in toluene (10 mL) was added 1 equiv of $[Mo(CO)_6]$ (61 mg, 0.23 mmol) and an excess of KOH (0.20 g, 3.56 mmol). The resulting suspension was stirred for 24 h. The solution was then filtered, and subsequently the solvent was evaporated to dryness. The residue was extracted with hexane (2 × 5 mL). The solution was filtered and then evaporated to dryness to give a white solid. Yield: 40 mg (33%). Anal. Calcd for C₂₂H₁₇N₂MoO₅P: C, 50.97; H, 3.31; N, 5.41. Found: C, 50.44; H, 3.62; N, 5.01. ¹H NMR (300 MHz, CD₂Cl₂, 25 °C): δ 7.43–7.33 (m, 10 H, Ph), 6.35 (s, 1 H, ==CH), 3.78 (s, 3 H, NMe), 3.77 (s, 3 H, NMe). ¹³C{¹H} NMR (75.46 MHz, CD₂Cl₂, 25 °C): δ 212.6 (s, CO), 207.3 (s, CO), 192.9 (s, C2), 134.4–129.5 (Ph), 129.8 (s, CS), 40,4 (s, NMe), 38.9 (d, ³J(C,P) = 12.5 Hz, NMe). ³¹P{¹H} NMR (121.48 MHz, CD₂Cl₂, 25 °C): δ –33.4 (s, PPh₂). IR (CH₂Cl₂): ν (CO) 2063 (m), 1928 (vs) cm⁻¹. MS (FAB): *m/z* 518.0 [*M*]⁺.

Compound 12. To a solution of [3]OTf (0.1 g, 0.23 mmol) in toluene (10 mL) was added 1/2 equiv of $[Mo(CO)_6]$ (31 mg, 0.12 mmol) and an excess of KOH (0.20 g, 3.56 mmol). The resulting suspension was heated at 90 °C for 45 min. The solution was then filtered and the solvent evaporated to dryness. The residue was washed with hexane (2 × 10 mL) to give a pale yellow solid. Yield: 36 mg (40%). ¹H NMR (300 MHz, CD₂Cl₂, 25 °C): δ 7.46–7.27 (m, 20 H, Ph), 6.27 (s, 2 H, ==CH), 3.56 (s, 6 H, NMe), 3.47 (s, 6 H, NMe). ¹³C{¹H} NMR (75.46 MHz, CD₂Cl₂, 25 °C): δ 220.0 (s, CO), 212.0 (s, CO), 200.5 (s, C2), 134.6–128.0 (Ph), 129.1 (s, C5), 39,7 (s, NMe), 38.0 (d, ³*J*(C,P) = 11.7 Hz, NMe). ³¹P{¹H} NMR (121.48 MHz, CD₂Cl₂, 25 °C): δ –33.9 (s, PPh₂). IR (CH₂Cl₂): ν (CO) 1994 (m), 1868 (vs), 1830 (s) cm⁻¹. MS (FAB): *m/z* 770.1 [*M*]⁺.

Compound 13. ${}^{1}P{}^{1}H$ NMR (121.48 MHz, CH_2Cl_2/D_2O capillary, 25 °C): δ -33.7 (s, PPh₂).

Compound 14. IR (CH₂Cl₂): ν (CO) 2084 (s), 2003 (vs) cm⁻¹.

Compound 15. A solution containing compound 11 (20 mg, 0.039 mmol) and 1 equiv of $[Mo(CO)_6]$ (10 mg, 0.039 mmol) in toluene (6 mL) was heated at 108 °C for 1 h. The solvent was then evaporated to dryness under vacuum and the residue extracted with hexane $(2 \times 5 \text{ mL})$. The solution was then filtered and evaporated to dryness to afford a white solid. Crystals of 15 suitable for X-ray analysis were formed by slow diffusion of hexane into a dichloromethane solution of the compound. Yield: 27 mg, 93%. Anal. Calcd for C27H17N2M02O10P: C, 43.11; H, 2.28; N, 3.72. Found: C, 42.86; H, 2.42; N, 3.52. ¹H NMR (300 MHz, CD₂Cl₂, 25 °C): δ 7.57 (br, 10 H, Ph), 7.09 (d, ${}^{3}J(H,P) = 1.7$ Hz, 1 H, =CH), 3.91 (s, 3 H, NMe), 3.53 (s, 3 H, NMe). ¹³C{¹H} NMR (75.46 MHz, CD₂Cl₂, 25 °C): δ 212.3 (s, CO trans), 210.0 (d, ${}^{2}J(C,P) = 24.3$ Hz, CO trans), 206.9 (s, CO *cis*), 205.8 (d, ${}^{2}J(C,P) = 8.7$ Hz, CO *cis*), 197.9 (s, C2), 133.5–128.7 (Ph), 132.9 (d, ${}^{2}J(C,P) = 14.5$ Hz, C5), 125.9 (d, ${}^{1}J(C,P) = 28.8$ Hz, C4), 41,0 (s, NMe), 40.8 (d, ${}^{3}J(C,P) = 2.0 \text{ Hz}$, NMe). ${}^{31}P{}^{1}H{}$ NMR (121.48 MHz, CD₂Cl₂, 25 °C): δ 16.7 (s, PPh₂). IR (CH₂Cl₂): ν (CO) 2075 (m), 2064 (m), 1948 (vs), 1931 (vs) cm⁻¹. MS (FAB): m/z 755.8 [M]⁺.

Compound 16. To a solution of compound 11 (30 mg, 0.058 mmol) in CH_2Cl_2 (6 mL) was added 1/2 equiv of $[RuCl_2(p-cym)]_2$

(18 mg, 0.029 mmol) and the resulting mixture stirred for 15 min. The solvent was evaporated to dryness under vacuum, affording an orange solid which was washed with hexane (2 × 10 mL). Yield: 39 mg, 82%. ¹H NMR (300 MHz, CD₂Cl₂, 25 °C): δ 7.82–7.75 (m, 5 H, Ph), 7.78 (s, 1 H, ==CH), 7.53–7.46 (m, 5 H, Ph), 5.24 (d, ³J(H,H) = 5.8 Hz, 2 H, *p*-cym), 5.05 (d, ³J(H,H) = 5.8 Hz, 2 H, *p*-cym), 3.89 (s, 3 H, NMe), 3.31 (s, 3 H, NMe), 2.72 (m, 1 H, CHMe₂), 1.79 (s, 3 H, Me), 1.07 (d, ³J(H,H) = 6.9 Hz, 6 H, CHMe₂). ¹³C{¹H} NMR (75.46 MHz, CD₂Cl₂, 25 °C): δ 212.4 (s, CO *trans*), 207.0 (s, CO *cis*), 196.9 (s, C2), 138.3 (d, ²J(C,P) = 23.7 Hz, C5), 134.1–126.7 (Ph), 131.6 (d, ¹J(C,P) = 48.5 Hz, C4), 112.3 (s, *p*-cym), 97.2 (s, *p*-cym), 89.8 (d, ²J(C,P) = 1.8 Hz, *p*-cym), 87.6 (d, ²J(C,P) = 5.5 Hz, *p*-cym), 41,0(s, NMe), 31.0 (s, CHMe₂), 22.0 (s, CHMe₂), 18.0 (s, Me). ^{31P{1H}} NMR (121.48 MHz, CD₂Cl₂, 25 °C): δ 4.2 (s, PPh₂). IR (CH₂Cl₂): ν (CO) 2064 (m), 1929 (vs) cm⁻¹.

Compound 17. To a solution of [3]OTf (30 mg, 0.07 mmol) in THF (5 mL) was added 1 equiv of [RhCl(COD)]₂ (34 mg, 0.07 mmol). Then LiN(SiMe₃)₂ (70 mL of a 1 M hexane solution, 0.07 mmol) was added to the solution and the mixture stirred for 15 min. The solution was then filtered and the solvent evaporated to dryness to obtain an orange solid, which was washed with hexane $(2 \times 10 \text{ mL})$. Yield: 44 mg (82%). Anal. Calcd for C₃₃H₄₁N₂Cl₂PRh₂: C, 51.25; H, 5.34; N, 3.62. Found: C, 50.59; H, 4.81; N, 3.53. ¹H NMR (300 MHz, CD₂Cl₂, 25 °C): δ 7.45-7.217 (m, 10 H, Ph), 6.83 (s, 1 H, =CH), 5.56 (s, 2H, CH COD), 4.96 (s, 2 H, CH COD), 4.47 (s, 3 H, NMe), 4.02 (s, 3 H, NMe), 3.49 (s, 1 H, CH COD), 3.37 (s, 2 H, CH COD), 3.00 (s, 1 H, CH COD), 2.39 (s, 8H, CH₂ COD), 1.98 (s, 4H, CH₂ COD), 1.95 (s, 4H, CH₂ COD). ¹³C{¹H} NMR (75.46 MHz, CD₂Cl₂, 25 °C): δ 189.7 (d, ¹*J*(C,Rh) = 51 Hz, C2), 138.4–128.7 (Ph), 130.5 $(d, {}^{2}J(C,P) = 19.2, C5), 125.8 (d, {}^{1}J(C,P) = 54.5 Hz, C4), 106.9-$ 106.3 (CH COD), 99.0 (t, J = 6.7 Hz, CH COD), 73.1 (d, ${}^{1}J(C,Rh) =$ 13.3 Hz, CH COD), 71.2 (d, ${}^{1}J(C,Rh) = 13.3$ Hz, CH COD), 68.8 (t, J = 15.6 Hz, CH COD), 39,6 (s, NMe), 38.3 (s, NMe), 33.3 (s, CH₂ COD), 29.5 (s, CH₂ COD), 29.4 (s, CH₂ COD). ³¹P{¹H} NMR $(121.48 \text{ MHz}, \text{CD}_2\text{Cl}_2, 25 \text{ °C}): \delta 9.1 (d_1^{-1}J(\text{Rh},\text{P}) = 151.5 \text{ Hz}, \text{PPh}_2).$ MS (FAB): m/z 773.3 $[M]^+$.

Generation of Compound 18. Complex 18 was readily formed by bubbling carbon monoxide through a solution of 17 in CH₂Cl₂ for 5 min. ³¹P{¹H} NMR (121.48 MHz, CH₂Cl₂/D₂O capillary; 25 °C): δ 11.0 (d, ¹J(Rh,P) = 128.8 Hz, PPh₂). IR (CH₂Cl₂): ν (CO) 2100 (s), 2084 (s), 2018 (s), 2004 (vs) cm⁻¹.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.5b00722.

NMR spectra for the new compounds (PDF) Crystallographic data for compounds [3]OTf, [10]-(OTf)₂, and 15 (CIF)

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Notes

The authors declare no competing financial interest.

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