

Activation of a 1,10-phenanthroline ligand on a rhenium tricarbonyl complex†

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The reactions of complex $[\text{Re}(\text{PPh}_2)(\text{CO})_3(\text{phen})]$ with either methyl acrylate or methyl propiolate afford products in which the phen ligand has been activated.

2,2'-Bipyridine (bipy), 1,10-phenanthroline (phen) and their substituted analogues form robust metal complexes that have played important roles in several areas of chemistry.^{1–3} Coordinated bipy and phen are so inert that the nucleophilic attack of hydroxide anion on a N-adjacent carbon, proposed to explain the anomalous behaviour of some bipy or phen complexes,⁴ is discussed in textbooks⁵ and continues to attract interest while remaining controversial.^{6,7}

We have recently found that complexes $[\text{MoY}(\eta^3\text{-allyl})(\text{CO})_2(\text{N-N})]$ and $[\text{ReY}(\text{CO})_3(\text{N-N})]$ (Y = alkoxo, hydroxo or amido; N–N = bipy or phen) react with dimethylacetylene dicarboxylate (DMAD).^{8–11} The results are consistent with initial attack by the Y ligand at one of the acetylenic carbon atoms and addition of the putative resulting vinyl carbanion to either the metal (for M–OR complexes with displacement of oxygen) or a CO ligand (hydroxo or amido complexes). These results are depicted in Scheme 1.

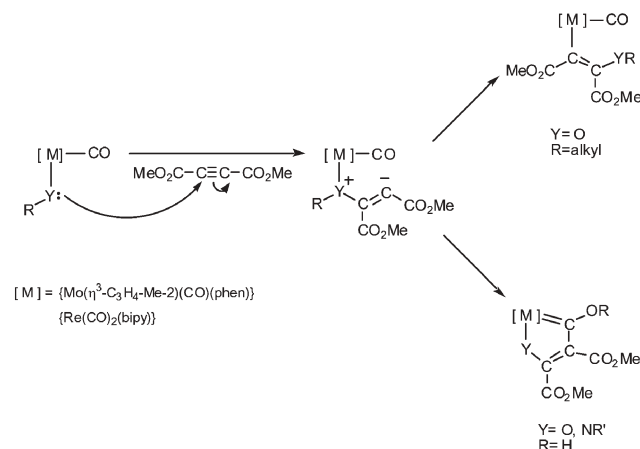
We also reported the synthesis and highly nucleophilic character of the phosphido complex $[\text{Re}(\text{PPh}_2)(\text{CO})_3(\text{phen})]$ (**1**).¹² Studies of the reactivity of terminal phosphido complexes are scarce.^{13–16} Here we report that **1** reacts with electron-poor olefinic or

acetylenic substrates to afford products resulting from addition to the N-adjacent carbon of phen.

The phosphido complex **1** was found to react with methyl acrylate and with methyl propiolate, affording the new compounds **2** and **3**, respectively, as the single products (see Scheme 2).^{17,18} These products could be isolated in high yield and characterized both in solution by IR and NMR (¹H, ¹³C and ³¹P) spectroscopies and in solid state by single-crystal X-ray diffraction. The IR spectra indicated the persistence of *fac*-Re(CO)₃ moieties in **2** and **3**, thus ruling out intramolecular attack on one of the carbonyl ligands, as have been found in the reactions of hydroxo and amido complexes with DMAD (see above) and in previous studies of the reactivity of iron, molybdenum and tungsten phosphido complexes. The observation of coupling to phosphorus in the signals of the carbonyl ligands in the ¹³C NMR spectra strongly suggests that the Re–P bond also remains intact. The ¹H NMR spectra revealed the desymmetrization of the phenanthroline ligand. These features are consistent with the solid-state structures, showed in Figs. 1 (compound **2**) and 2 (compound **3**).‡

The molecules of **2** and **3** are distorted octahedra consisting of *fac*-Re(CO)₃ moieties bonded to the asymmetric PNN' donor set of a new tridentate ligand in which the C₂ unit from the olefin or acetylene links the phosphorus atom to the C2 atom of the phen backbone thus creating a six-membered metallacycle. The loss of aromaticity in the phen ring attacked resulted in its distortion from planarity. The phosphorus is bonded to the non-substituted atom of the olefin or acetylene, a fact consistent with the mechanistic proposal (in line with our previous studies on the reactivity of alkoxo, hydroxo and amido complexes) shown in Scheme 3, since the nucleophilic phosphido group would attack the more electrophilic carbon of the organic substrate. The bonding scheme depicted for the attacked phen ring of the product in Scheme 3 is substantiated by the comparison of the intraligand distances in **1** (in Å, numbering scheme as for **2** and **3**: N(1)–C(11) 1.327(11), C(11)–C(12) 1.387(15), C(12)–C(13) 1.354(17)) with those found in **2** and **3** (see captions of Figs. 1 and 2).

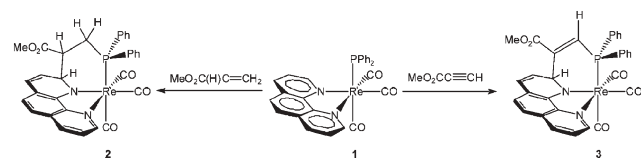
In summary, we have presented evidence of two reactions resulting in the activation of a phenanthroline ligand under very mild conditions, a transformation without precedents in the



Scheme 1

† Electronic supplementary information (ESI) available: General experimental details and atom-labeling scheme for phen'. See <http://www.rsc.org/suppdata/cc/b4/b412447b/>

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Scheme 2

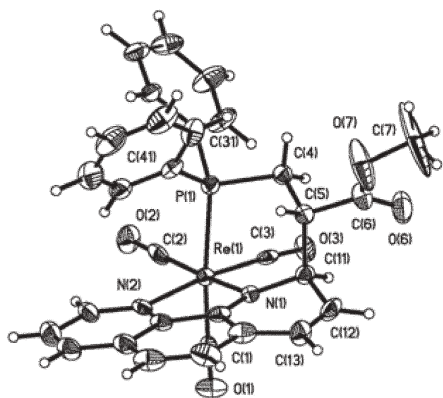


Fig. 1 Thermal ellipsoid (30%) plot of **2**. Selected bond lengths (Å): N(1)–C(11) 1.452(11), C(11)–C(12) 1.540(14), C(12)–C(13) 1.307(14).

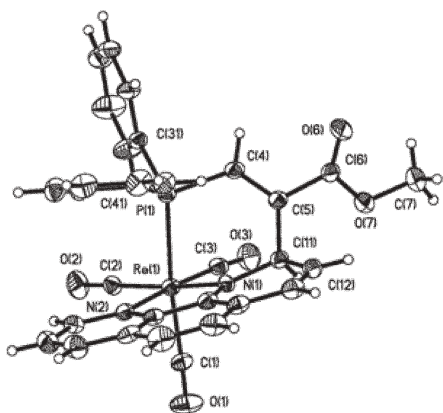
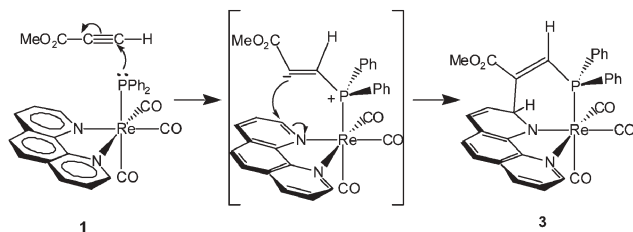


Fig. 2 Thermal ellipsoid (30%) plot of **3**. Selected bond lengths (Å): N(1)–C(11) 1.469(8), C(11)–C(12) 1.522(9), C(12)–C(13) 1.321(10).



Scheme 3

chemistry of carbonyl complexes.¹⁹ Studies of the reactivity of **1** with other electrophiles are under way in our laboratory.

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Notes and references

† CCDC reference numbers 246293 (**2**) and 246294 (**3**). See <http://www.rsc.org/suppdata/cc/b4/b412447b/> for crystallographic data in .cif or other electronic format.

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- Synthesis of 2**: Methyl acrylate (11 μ L, 0.13 mmol) was added to a solution of **1** (0.081 g, 0.13 mmol) in THF (10 mL). The colour of the solution immediately changed from blue to red. The solution was stirred for 20 h, *in vacuo* concentration and precipitation with hexane afforded a red microcrystalline solid. Slow evaporation of a concentrated solution of **2** in diethyl ether–CH₂Cl₂ afforded crystals of good quality for an X-ray determination. Yield: 0.079 g, 84%. Anal. Calc. for C₃₁H₂₄N₂O₅PRe: C, 51.59; H, 3.35; N, 3.88. Found: C, 51.42; H, 3.52; N, 3.93%. IR (THF): 2014, 1920, 1892 (ν_{CO}). ¹H NMR (C₆D₆): δ 8.15 [m, 1H], 7.53 [m, 1H], 7.01–6.94 [m, 6H], 6.76–6.65 [m, 3H], 6.56 [m, 1H], 6.41 [m, 3H], 6.12 [dd (8.54, 5.13), 1H], 6.03 [d (7.97), 1H], 5.30 [m, 2H], 3.84 [m, 1H], 3.33 [s, 3H, Me], 2.97 [m, 1H], 2.78 [m, 1H]. ¹³C{¹H} NMR (C₆D₆): δ 198.9 [t (9.44), ReCO], 191.9 [d (74.79) ReCO], 172.9 [d (12.84 Hz), CO₂Me] 155.4, [s, phen'], 148.2, 146.7, 136.7, 135.9, 135.4, 134.2, 132.5, 131.7, 127.0, 125.8, 121.9 [phen' and Ph], 115.6, 107.3 [s, C3, C4 phen'], 68.4 [s, C5 phen'], 52.1 [s, CO₂CH₃], 49.3 [s, PCH₂C(H)CO₂Me], 32.9 [d (27.95 Hz), PCH₂]. ³¹P{¹H} NMR (C₆D₆): δ –0.86.
- Synthesis of 3**: Methyl propionate (8 μ L, 0.09 mmol) was added to a solution of **1** (0.050 g, 0.08 mmol) in THF (10 mL) causing a colour change from blue to red. The mixture was stirred for 5 min and a microcrystalline solid was obtained by addition of hexane. The solid was dissolved in CH₂Cl₂ and filtered through alumina (activation grade IV). The solution was concentrated *in vacuo*, layered with hexane and stored at –20 °C, affording purple crystals, one of which was used for the X-ray structure determination. Yield: 0.047 g, 81%. Anal. Calc. for C₃₁H₂₂N₂O₅PRe: C, 51.74; H, 3.08; N, 3.89. Found: C, 51.22; H, 3.02; N, 3.94%. IR (THF): 2015, 1922, 1896 (ν_{CO}). ¹H NMR (C₆D₆): δ 8.13 [m, 1H], 7.27 [m, 1H], 7.00 [m, 4H], 6.87 [dt (8.54, 1.42), 1H], 6.72 [m, 2H], 6.60–6.57 [m, 2H], 6.47–6.42 [m, 3H], 6.25 [dd (9.68, 1.42), 1H], 6.03 [dd (8.25, 4.84), 1H], 5.09 [d (8.25) 1H], 5.51 [dd (9.68, 4.84), 1H], 3.27 [s, 3H, Me]. ¹³C{¹H} NMR (CD₂Cl₂): δ 198.3 [d (6.5), ReCO], 196.9 [d (8.1), ReCO], 193.0 [d (75.09), ReCO], 167.5 [d (15.34), CO₂Me], 156.7, 156.3, 147.6, 144.7, 136.6, 1 [s, phen'], 134.7, [d (12.1), C1], 132.6, [d (11.3), C2], 131.7, [s, phen'], 129.5 [d (7.3), Ph], 129.1 [d (10.4), Ph], 128.6, [s, phen'], 127.9 [d (9.7 Hz), Ph], 127.8 [s, Ph], 127.3, 121.9, 119.8, [s, phen'], 114.3, 107.7 [s, C3, C4 phen'], 64.7 [s, C5 phen'], 52.6 [s, CO₂CH₃]. ³¹P{¹H} NMR (C₆D₆): δ 3.41.
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