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Activation of Ancillary Ligands in the Reactions of DMAD with Phosphido and Alkylideneamido Rhenium Complexes

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*Summary: As an extension of previous work, the reactions of dimethylacetylenedicarboxylate (DMAD) with the phosphido complex [Re(PPh$_2$)(CO)$_3$(phen)] (**1**) and the alkylideneamido [Re(N=CPh$_2$)(CO)$_3$(bipy)] (**2**) were investigated. The characterization of the products by spectroscopy (IR and NMR) and X-ray diffraction revealed the coupling between DMAD, the phosphido or alkylideneamido group, and the phenanthroline (in the reaction of **1**) or one of the carbonyl (in the reaction of **2**) ligands, in a way consistent with initial attack of the P in **1** (or the N in **2**) on one of the acetylenic carbons of DMAD.*

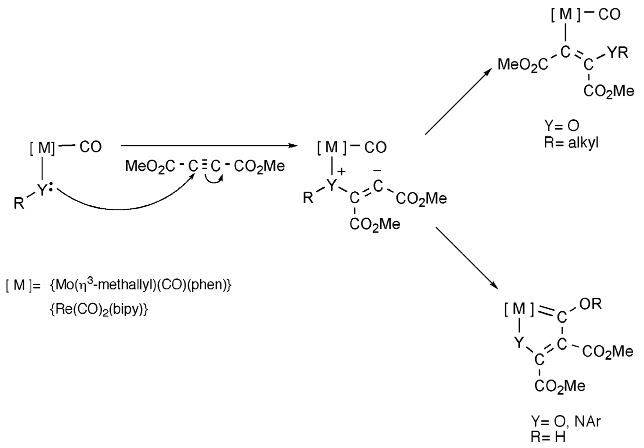
Introduction

We have recently studied the reactivity of electron-poor acetylenes toward molybdenum and rhenium complexes of the types [Mo(η^3-allyl)X(CO)$_2$(N−N)] and [ReX(CO)$_3$(N−N)] (X = OR, OH, N(H)Ar; N−N = 2, 2′-bipyridine (bipy), 1,10-phenanthroline (phen)).[1] The reactions with alkoxo complexes yield the products of the formal insertion of the acetylene into the M−OR bond.[1a] In contrast, metallacyclic hydroxycarbenes are obtained in the reactions of the hydroxo and amido complexes,[1b,c] as the result of (a) the involvement of one of the carbonyl ligands and (b) the hydrogen migration from the O−H or N−H bond to the carbonyl oxygen (see Scheme 1). This rich reactivity prompted us to extend our studies to two other complexes containing strongly nucleophilic ligands, namely, the phosphido [Re(PPh$_2$)(CO)$_3$(phen)][2] (**1**) and the alkylideneamido complex [Re(N=CPh$_2$)(CO)$_3$(bipy)][3] (**2**). Our results are the subject of the present contribution.

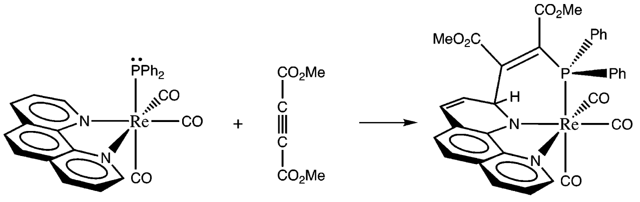
Results and Discussion

Complex **1** reacted instantaneously with an equimolar amount of DMAD, as indicated by the color change from blue to red, to afford the new compound **3** (see Scheme 2) as a single product. IR and NMR (^{1}H and ^{31}P) monitoring of the reaction indicated a quantitative transformation.

Scheme 1



Scheme 2



Complex **3** was characterized by means of IR and NMR spectroscopies in solution and by single-crystal X-ray diffraction in the solid state (see Figure 1).

This reaction, implying the activation of the phen ligand, is analogous to that of **1** with methyl propiolate to afford **4** (see Scheme 3), recently reported by us,[1d] and therefore neither the structure of the product nor the plausible mechanism will be further discussed here.

There is, however, an important difference between the products of the two reactions. Thus, whereas **4** is indefinitely stable in solution at room temperature, ^{31}P NMR monitoring of a THF solution of complex **3** at room temperature showed its slow (5 days) transformation into a new compound, **5**, characterized by a singlet at 25.4 ppm (the resonance of **3** occurs at 7.1 ppm). The reaction could also be monitored by IR spectroscopy

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(1) (a) Hevia, E.; Pérez, J.; Riera, L.; Riera, V.; Miguel D. *Organometallics* **2002**, *21,* 1750−1752. (b) Hevia, E.; Pérez, J.; Riera, V.; Miguel, D.; *Organometallics* **2003**, *22*, 257−263. (c) Cuesta, L.; Gerbino, D. C.; Hevia, E. Morales, D.; Navarro Clemente, M. E.; Pérez, J.; Riera, L.; Riera, V.; Miguel, D.; del Río, I.; García-Granda, S. *Chem. Eur. J.* **2004**, *10*, 1765−1777. (d) Cuesta, L.; Hevia, E.; Morales, D.; Pérez, J.; Riera, V.; Rodríguez, E.; Miguel, D. *Chem. Commun.* **2005**, 116−117.

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10.1021/om049019r CCC: $30.25

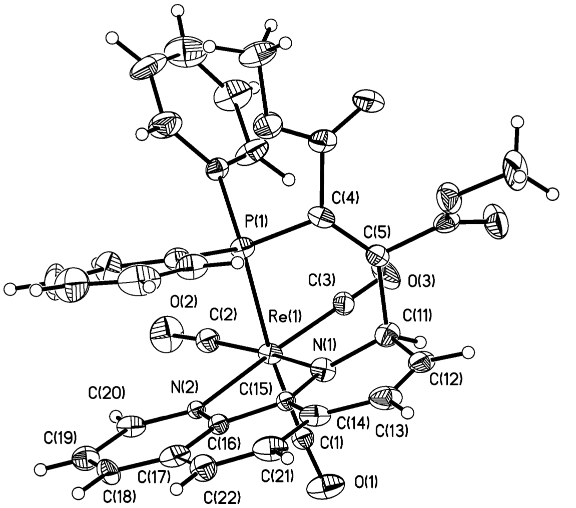
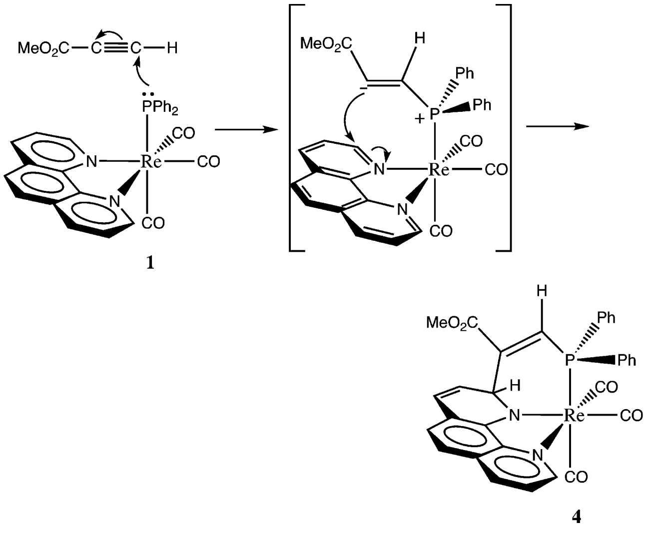


Figure 1. Thermal ellipsoid (30%) plot of **3**. Selected bond lengths (Å): Re(1)−C(2) 1.90(2), Re(1)−C(1) 1.944(18), Re(1)−C(3) 1.965(19), Re(1)−N(1) 2.146(14), Re(1)−N(2) 2.193(12), Re(1)−P(1) 2.475(5). Selected bond angles (deg): C(2)−Re(1)−C(1) 89.2(8), C(2)−Re(1)−C(3) 90.6(8), C(1)−Re(1)−C(3) 88.4(7), C(2)−Re(1)−N(1) 169.2(7), C(1)−Re(1)−N(1) 95.7(6), C(3)−Re(1)−N(1) 99.1(7), C(2)−Re(1)−N(2) 95.9(6), C(1)−Re(1)−N(2) 92.4(7), C(3)−Re(1)−N(2) 173.5(6), N(1)−Re(1)−N(2) 74.4(5), C(2)−Re(1)−P(1) 98.7(6), C(1)−Re(1)−P(1) 171.9(5), C(3)−Re(1)−P(1) 90.2(5), N(1)−Re(1)−P(1) 76.7(4), N(2)−Re(1)−P(1) 88.1(3).

Scheme 3



using the shift of the ν(CO) bands, from 2017, 1923, and 1896 cm^{-1} in **3** to 2024, 1931, and 1904 cm^{-1} in **5**. The IR pattern indicates the persistence of the {*fac*-Re(CO)$_3$} moiety, whereas the small magnitude of the shift suggests a small change in the electron density at the metal and, therefore, that processes such as changes in the oxidation state of the metal or in the charge of the complex can be ruled out. The structure of **5** in the solid state was determined by X-ray diffraction, and the results, shown in Figure 2, are in agreement with the spectroscopic data in solution.

The transformation of **3** into **5** consists of a 1,3-migration of hydrogen from the C$_2$ carbon of the dearomatized ring originating from the phen ligand to the P-bonded carbon atom originating from DMAD (see Scheme 4).

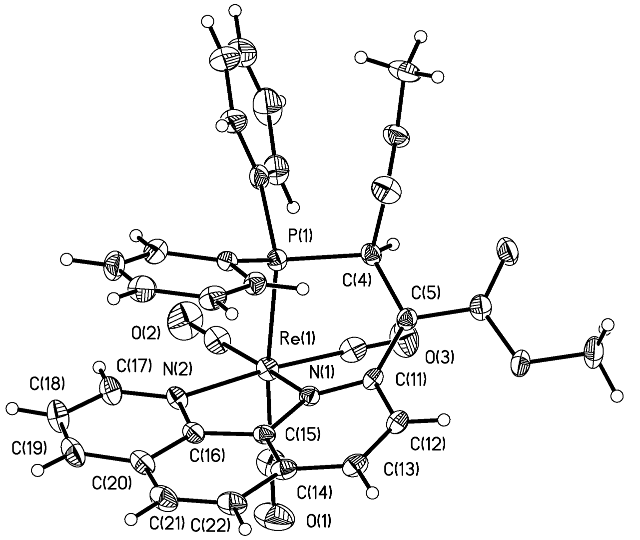
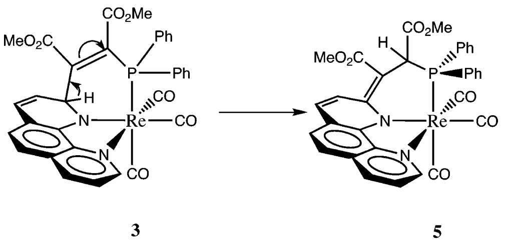


Figure 2. Thermal ellipsoid (30%) plot of **5**. Selected bond lengths (Å): Re(1)−C(2) 1.902(6), Re(1)−C(1) 1.960(6), Re(1)−C(3) 1.919(5), Re(1)−N(1) 2.179(4), Re(1)−N(2) 2.172(3), Re(1)−P(1) 2.4362(12). Selected bond angles (deg): C(2)−Re(1)−C(1) 89.6(2), C(2)−Re(1)−C(3) 90.0(2), C(1)−Re(1)−C(3) 88.5(2), C(2)−Re(1)−N(1) 170.05(18), C(1)−Re(1)−N(1) 95.64(19), C(3)−Re(1)−N(1) 98.54(17), C(2)−Re(1)−N(2) 95.90(18), C(1)−Re(1)−N(2) 95.64(19), C(3)−Re(1)−N(2) 173.74(18), N(1)−Re(1)−N(2) 75.74(13), C(2)−Re(1)−P(1) 100.11(17), C(1)−Re(1)−P(1) 170.17(17), C(3)−Re(1)−P(1) 89.79(15), N(1)−Re(1)−P(1) 75.04(10), N(2)−Re(1)−P(1) 91.13(10), N(1)−C(11)−C(5) 120.2(4).

Scheme 4



In the ^{1}H NMR spectrum of **5**, this hydrogen atom appears (at 4.47 ppm in CD$_2$Cl$_2$) as a doublet (J = 11.56 Hz) due to the coupling with phosphorus. Concomitantly with the H migration, there is a change in the position of the carbon−carbon double bond (originally resulting from the insertion of the acetylenic unit), which in **5** becomes part of the conjugated system. The driving force of the transformation of **3** into **5** can, at least in part, be traced to this increase in the conjugation. On the other hand, the electron flow depicted in Scheme 4, associated with a H$^+$ transfer, allows us to rationalize why complex **4**, lacking the strongly electron-withdrawing methoxycarbonyl substituent on the P-bonded carbon, does not undergo an analogous transformation. Treatment of a THF solution of complex **3** with an equimolar amount of n-butyllithium resulted in a large shift to lower wavenumber values in the IR spectrum, suggesting deprotonation of the complex. Addition of trifluoromethanesulfonic acid to the resulting solution led to the immediate formation of **5**. These results lend additional support to our depiction of the **3**-to-**5** transformation as a proton (rather than hydride or radical) migration.

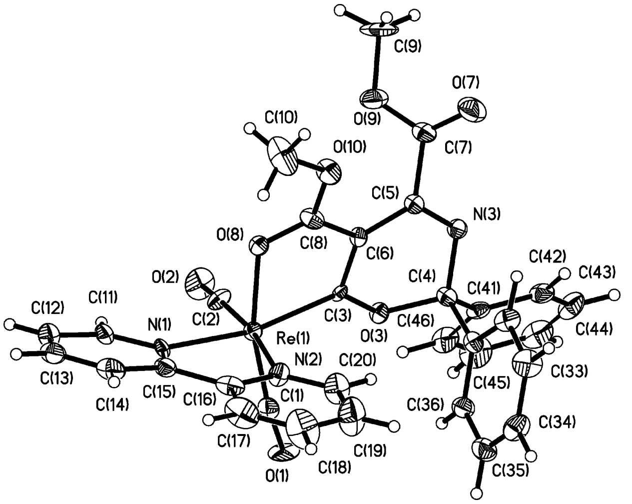
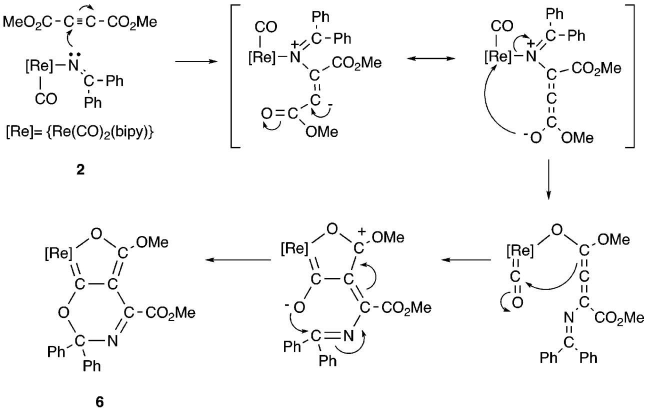


Figure 3. Thermal ellipsoid (30%) plot of **6**. Selected bond lengths (Å): Re(1)−C(1) 1.903(11), Re(1)−C(2) 1.927(11), Re(1)−C(3) 2.023(8), Re(1)−N(1) 2.176(7), Re(1)−N(2) 2.189(8), Re(1)−O(8) 2.208(6). Selected bond angles (deg): C(1)−Re(1)−C(2) 84.4(4), C(1)−Re(1)−C(3) 93.2(4), C(2)−Re(1)−C(3) 89.5(4), C(1)−Re(1)−N(1) 104.7(3), C(1)−Re(1)−N(1) 98.4(4), C(3)−Re(1)−N(1) 161.0(3), C(1)−Re(1)−N(2) 172.2(4), C(2)−Re(1)−N(2) 172.2(4), C(3)−Re(1)−O(8) 77.0(3), O(3)−C(3)−Re(1) 126.8(7), C(6)−C(3)−Re(1) 116.7(6), C(8)−O(8)−Re(1) 111.4(6).

Scheme 5



The alkylideneamido complex [Re(N=CPh$_2$)(CO)$_3$(bipy)] (**2**) reacted instantaneously with an equimolar amount of DMAD to yield the new metallacycle compound **6**, as shown in Scheme 5, where a mechanistic proposal is sketched.

The reaction was monitored both by IR (in THF) and ^{1}H NMR (in CD$_2$Cl$_2$), being found to be quantitative. The IR spectrum of **6**, featuring two similarly intense ν_{CO} absorptions, was consistent with the presence of a *cis*-dicarbonyl moiety. *cis*-Dicarbonyl rhenium complexes have been previously obtained as the products of the reactions of [ReX(CO)$_3$(N−N)] (X = hydroxo, amido) complexes with DMAD (see above).[1b,c] However, the lack of a hydrogen atom on the metal-bonded heteroatom of the alkylideneamido ligand of the precursor **2** implies that a different mechanism must be involved in the formation of **6**. The structure of the product could not be inferred from the spectroscopic data alone. A single crystal of complex **6** was subjected to a X-ray diffraction analysis, with the results summarized in Figure 3.

The molecule of **6** consist of a {*cis*-Re(CO)$_2$(bipy)} moiety bound to the carbon and oxygen atoms (C(3) and O(8) in Figure 3) of a ligand resulting from the coupling of the alkylideneamido ligand, one of the carbonyl ligands, and DMAD. The bond distances are consistent with the bond orders depicted in Scheme 5. The ability of complex **2** to get involved in insertion and cycloaddition processes has been previously demonstrated in the reactions of **2** with isocyanates[3] and with ketenes.[4] A new feature of the reaction of **2** with DMAD to afford **6** is that one of the CO ligands of **2** also takes part in the transformation.

In summary, the reactions of DMAD with the phosphido complex **1** and with the alkylideneamido **2** provide examples of couplings involving activation of phenanthroline or CO ligands.

Experimental Section

General conditions were given elsewhere.[2] In the following, phen′ designates the substructure (within the new tridentate ligand) originated from phenanthroline.

X-ray Structures. Data in common: Bruker AXS SMART 1000 CCD diffractometer, ϕ and ω scans, Mo Kα radiation (λ 0.71073 Å), graphite monochromator, $T = 295$ K. Raw frame data were integrated with the SAINT[5] program. Structures were solved by direct methods with SHELXTL;[6] semiempirical absorption correction with SADABS.[7] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were set in calculated positions and refined as riding atoms, with a common thermal parameter. All calculations were made with SHELXTL.

Synthesis of 3. DMAD (10 μL, 0.081 mmol) was added to a solution of **1** (0.050 g, 0.080 mmol) in THF (10 mL). The color of the solution changed instantaneously from blue to red. The solvent was removed under vacuum, and the solid was redissolved in CH$_2$Cl$_2$ and filtered through alumina (activation grade IV). The solution was concentrated to 10 mL, layered with hexane (10 mL), and stored at −20 °C, affording purple crystals suitable for an X-ray determination. Yield: 81% (0.044 g). Anal. Calcd for C$_{33}$H$_{24}$N$_2$O$_7$PRe·0.5CH$_2$Cl$_2$: C, 49.06; H, 3.07; N, 3.14. Found: C, 49.22; H, 2.97; N, 3.21. IR (ν_{CO}) (CH$_2$Cl$_2$): 2017 (vs), 1923 (s), 1896 (s). ^{1}H NMR (CD$_2$Cl$_2$): 8.40 [m, 1H], 7.53−7.34 [m, 2H], 6.99−6.78 [m, 6H], 6.59 [d(8.0), 1H], 6.32−6.29 [m, 2H], 6.01 [d(7.7), 1H], 4.99 [dd(9.4, 4.8)], 3.78 [s, 3H, Me], 3.02 [s, 3H, Me]. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): 197.7 [d(7.2), Re-*C*O], 197.3 [d(6.5), Re-*C*O], 193 [d(17.1), Re-*C*O], 167.2 [d(12.9), *C*O$_2$Me], 166.1 [s, phen′], 156.4 [d(4.9), *C*O$_2$Me], 156.2, 147.9, 144.5, 136.9 [s, phen′], 135.4 [d(12.9), P*C*(CO$_2$Me)], 132.8 [d(11.1),PC=*C*(CO$_2$Me)], 132.0, 131.6 [s, phen′], 130.4 [d(12.1), Ph], 130.0 [s, phen′], 128.8 [d(4.6), Ph], 127.6 [d(10.2), Ph], 127.3 [s, Ph], 122.1, 119.4 [s, phen′], 112.1, 108.3 [s, phen′], 66.1, 52.3 [s, Me]. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): 7.09.

Synthesis of 5. A solution of **3** (0.040 g, 0.056 mmol) in CH$_2$Cl$_2$ was stirred for 5 days at room temperature. Slow diffusion of hexane into a concentrated solution of **5** at −20 °C afforded purple crystals, one of which was used for the X-ray structure determination. Yield: 98% (0.031 g). Anal. Calcd for C$_{33}$H$_{24}$N$_2$O$_7$PRe·CH$_2$Cl$_2$: C, 47.33; H, 3.03; N, 3.24. Found: C, 47.22; H, 3.07; N, 3.11. IR (ν_{CO}) (CH$_2$Cl$_2$): 2024 (vs),

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(4) Hevia, E.; Pérez, J.; Riera, V.; Miguel, D. *J Am. Chem. Soc.* **2003**, *125,* 3706−3707.

(5) *SAINT*+, SAX area detector integration program, Version 6.02; Bruker AXS, Inc.: Madison, WI, 1999.

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(7) Sheldrick, G. M. *SADABS*, Empirical Absorption Correction Progam; University of Göttingen: Germany, 1997.

1931 (s), 1904 (s). ^{1}H NMR (CD_2Cl_2): 8.85 [m, 1H], 8.75, [m, 1H], 8.11 [m, 1H], 7.96−7.48 [m, 8H], 7.36 [dd(8.25, 4.96), 1H], 7.21 [d(8.42), 1H], 6.82−6.67 [m, 2H], 6.59−6.41 [m, 2H], 4.47 [d(11.56), 1H, PC(*H*)(CO_2Me)], 3.69 [s, 3H, Me], 3.21 [s, 3H, Me]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 199.1 [m, Re-*C*O], 196.4 [d(16.1), Re-*C*O], 172.3 [d(7.1), *C*O$_2$Me], 167.4 [d(10.3), *C*O$_2$Me], 166.1, 154.3, 153.8, 153.0, 151.1, 148.5, 146.5, 137.6 [s, phen′], 134.6 [d(14.2),PC-*C*(CO_2Me)], 132.6 [d(10.2), phen′], 131.9 [s, phen′], 130.1−126.4 [m, Ph], 124.7, 122.8, 119.3 [s, phen′], 52.3 [d(26.5), P*C*(CO_2Me)(H)], 51.8, 50.5 [s, Me]. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 25.41.

Synthesis of 6. DMAD (6 μL, 0.05 mmol) was added to a solution of **2** (0.030 g, 0.05 mmol) in THF (10 mL). The color of the solution changed instantaneously from dark green to red. The solvent was removed under vacuum, and the red solid was redissolved in CH_2Cl_2 (10 mL). Slow diffusion of hexane into this solution at −20 °C afforded red crystals of **6**. Yield: 83% (0.031 g). Anal. Calcd for $C_{32}H_{24}N_3O_7Re$: C, 51.33; H, 3.23; N, 5.61. Found: C, 51.72; H, 2.17; N, 5.81. IR (ν_{CO}) (THF): 1919 (vs), 1845 (s). ^{1}H NMR (CD_2Cl_2): 9.29 [m, 1H, bipy], 8.18−8.13 [m, 2H, bipy], 8.02−7.15 [m, 15 H, bipy and Ph], 3.78 [s, 3H, Me], 3.38 [s, 3H, Me]. $^{13}C\{^1H\}$ NMR(CD_2Cl_2): 256.0 [s, Re=*C*], 203.2 [s, Re-*C*O], 179.4 [s, Re-*C*O], 166.7 [s, Re-O*C*(OMe)], 156.9, 155.3, 154.8, 152.8 [s, bipy], 151.2 [s, *C*o$_2$Me], 145.9 [s, N=*C*(CO_2Me)], 145.3 [s, Re=C(O)-*C*], 138.7, 137.4, 129.8, 129.1 [s, bipy], 128.6, 128.5, 128.3, 128.0, 127.8, 127.2, 127.2, 127.1, 127.0, [s, Ph], 123.1, 122.45, [s, bipy], 106.5, 103.1, [s, Ph], 95.5 [s, O-*C*(Ph_2)-N], 53.3 [s, CO_2CH_3], 52.4 [s, O*C*H$_3$].

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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