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Synthesis of Rhenium(V) 2,4,6-Trimethylbenzylidyne Complexes by Abstracting "O^{2-}" from an Acyl with Triflic Anhydride

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Summary: *Re[C(O)Ar′](CO)$_5$ (Ar′ = 2,4,6-$C_6H_2Me_3$; 1) can be prepared in 55% yield by adding Ar′C(O)Cl to $[Re(CO)_5]^-$. Addition of trifluoromethanesulfonic anhydride to 1 in dichloromethane yields off-white [Re(CAr′)(CO)$_4$(OTf)](OTf) (2) quantitatively. Three equivalents of tetraethylammonium chloride reacts with 2 in dichloromethane to give [Et_4N][Re(CAr′)(CO)$_2$$Cl_3$] (3), which when treated with $TlBF_4$ in the presence of pyridine affords lemon yellow Re(CAr′)(CO)$_2$$Cl_2$(py) (4). A slurry of 2 in dichloromethane also reacts cleanly with a THF solution of LiO-2,6-C_6H_3-i-Pr_2 (LiOAr) to yield blood red Re(CAr′)(CO)$_2$(OAr)$_2$(THF) (**5a**) in 80% isolated yield. Addition of pyridine to **5a** yields an analogous six-coordinate pyridine adduct (**5b**). Addition of pinacol to 2 followed by triethylamine yields yellow, pentane-soluble Re(CAr′)(CO)$_2$($O_2C_2Me_4$) (**6a**). Although **6a** shows no tendency to bind THF, it reacts with pyridine to yield Re(CAr′)(CO)$_2$($O_2C_2Me_4$)(py) (**6b**) quantitatively. Addition of triphenylphosphine to **6a** produces dark red Re(CAr′)(CO)($O_2C_2Me_4$)(PPh_3) (**6c**).*

Introduction

Rhenium(VII) alkylidene alkylidyne complexes were first prepared more than 10 years ago.[1,2] Re(CR)(CHR)(OR′)$_2$ derivatives[3] (R = CMe_3 or CMe_2Ph) have proven to be useful for the metathesis of internal olefins,[4,5] but "reduction" via a "3+2 cycloaddition" reaction takes place in the presence of ethylene.[6] In order to explore the extent to which the reactivity of Re(CR)(CHR)(OR′)$_2$ derivatives is altered by the steric and electronic nature of the R group in the alkylidyne ligand, we have been looking for a method of preparing Re(VII) complexes that contain a 2,6-disubstituted benzylidyne ligand. Re(CR)(CHR)(OR′)$_2$ complexes that contain a (2,6-diisopropylphenyl)benzylidyne ligand would be isoelectronic with tungsten and molybdenum complexes of the type M(NAr)(CHR)(OR′)$_2$[7] that contain a (2,6-diisopropyl)phenylimido (NAr) ligand. Recent syntheses of rhenium alkylidene alkylidyne complexes, although they are more efficient than the original syntheses, are still variations of the original approach that (so far) have been successful only for the synthesis of neopentylidyne or neophylidyne complexes.

An alternative approach to Re(VII) alkylidyne complexes is to oxidize lower oxidation state species. Tungsten and molybdenum alkylidyne complexes in which the metal is in a +4 oxidation state (counting the alkylidyne as a trianionic ligand) have been oxidized to d^0 species,[8-10] as have ReCp* alkylidyne complexes.[11] We felt that if we could prepare a low oxidation state rhenium benzylidyne complex, it might prove possible to oxidize it to a d^0 alkylidyne complex. We report here the synthesis of d^2 rhenium 2,4,6-trimethylbenzylidyne complexes by "O^{2-} abstraction" from (2,4,6-trimethylbenzoyl)rhenium pentacarbonyl. Although it has not yet proved possible to oxidize the d^2 rhenium alkylidyne complexes to d^0 species, we believe that such species are of interest in their own right since they extend the family of rhenium(V) complexes that contain multiple metal—ligand bonds (Re═O, Re═NR, and Re≡N) and since mononuclear low oxidation state rhenium alkylidyne complexes that do not contain a cyclopentadienyl ligand are relatively rare.[10,12-15]

Results and Discussion

Re[C(O)Ar′](CO)$_5$ (Ar′ = 2,4,6-$C_6H_2Me_3$; 1) can be prepared in a manner that is directly analogous to the method reported for the synthesis of Re[C(O)Me](CO)$_5$.[16] Addition of Ar′C(O)Cl to $[Re(CO)_5]^-$ yields 1 in approximately 55% yield, a yield that is comparable to that reported for Re[C(O)Me](CO)$_5$ (45%). Addition of trifluoromethanesulfonic anhydride to 1 in dichloromethane yields off-white, insoluble [Re(CAr′)(CO)$_4$(OTf)](OTf) (2) quantitatively upon evolution of CO. Unfortunately, the insolubility of 2 prevented NMR characterization, but analytical and IR data are totally consistent with its formulation. The possibility that no triflate is bound to the metal seems slim, since that complex would be a sixteen-electron dication. If the alkylidyne ligand is counted as a trianion, then the reaction shown in eq 1 is a four electron oxidation of Re(I) to Re(V). Attempts to deoxygenate 1 to give 2 using procedures pioneered by Mayr and co-workers (e.g., oxalyl chloride)[8-10] so far have not been successful.

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[1] Edwards, D. S.; Schrock, R. R. *J. Am. Chem. Soc.* **1982,** *104,* 6806.

[2] Edwards, D. S.; Biondi, L. V.; Ziller, J. W.; Churchill, M. R.; Schrock, R. R. *Organometallics* **1983,** *2,* 1505.

[3] Toreki, R.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1992,** *114,* 3367.

[4] Schrock, R. R.; Toreki, R.; Vaughan, G. A.; Farooq, A. In "*Transition-Metal Carbyne Complexes*"; Kreissl, F. R., Ed.; Kluwer Academic: Dordrecht, The Netherlands, 1992.

[5] Toreki, R.; Vaughan, G. A.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1993,** *115,* 127.

[6] Vaughan, G. A.; Toreki, R.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1993,** *115,* 2980.

[7] Feldman, J.; Schrock, R. R. *Prog. Inorg. Chem.* **1991,** *39,* 1.

[8] Mayr, A.; McDermott, G. A.; Dorries, A. M. *Organometallics* **1985,** *4,* 608.

[9] Mayr, A.; McDermott, G. A. *J. Am. Chem. Soc.* **1986,** *108,* 548.

[10] Mayr, A.; Hoffmeister, H. *Adv. Organomet. Chem.* **1991,** *32,* 227.

[11] Herrmann, W. A.; Felixberger, J. K.; Anwander, R.; Herdtweck, E.; Kiprof, P.; Riede, J. *Organometallics* **1990,** *9,* 1434.

[12] Warner, S.; Lippard, S. J. *Organometallics* **1989,** *8,* 228.

[13] Pombiero, A. J. L. In "*Transition-Metal Carbyne Complexes*"; Kreissl, F. R., Ed.; Kluwer Academic: Dordrecht, The Netherlands, 1992; p 105.

[14] Felixberger, J. K.; Kiprof, P.; Herdtweck, E.; Herrmann, W. A.; Jakobi, R.; Gütlich, P. *Angew. Chem., Int. Ed. Engl.* **1989,** *28,* 334.

[15] Kim, H. P.; Angelici, R. J. *Adv. Organomet. Chem.* **1987,** *27,* 51.

[16] Darst, K. P.; Lukehart, C. M.; Warfield, L. T.; Zeile, J. V. In *Inorganic Syntheses*; Busch, D. H., Ed.; Wiley-Interscience: New York, 1980; Vol. XX, pp 200.

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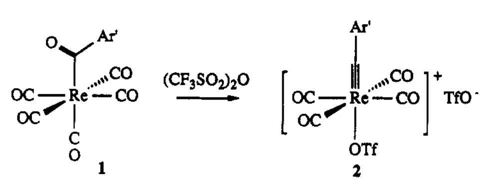
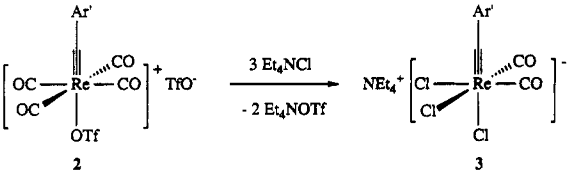


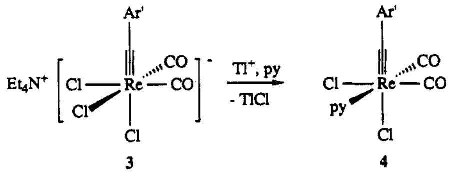
(1)

Three equivalents of tetraethylammonium chloride reacts cleanly with a slurry of **2** in dichloromethane over the course of 2 h to afford a pale yellow solution of **3** (eq 2). Unfortunately, **3** cannot be separated from the tetraethylammonium triflate coproduct, but the inability to purify **3** does not complicate subsequent reaction of it with $TlBF_4$ (see below). NMR and IR (2070 and 1978 cm^{-1}) spectra of **3** are not unusual. All data are consistent with the cis, *fac* configuration about rhenium that is shown in eq 2. One would expect the carbonyl ligands to be cis to the alkylidyne ligand in order to avoid competition between rhenium–carbonyl and rhenium–alkylidyne π bonds.



(2)

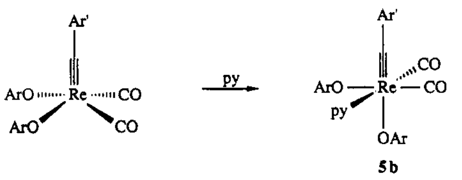
Addition of $TlBF_4$ to the mixture of **3** and tetraethylammonium triflate in dichloromethane in the presence of pyridine affords lemon yellow **4** (eq 3); this reaction can be done immediately after the reaction shown in eq 2. In the ^{13}C NMR spectrum of **4** the alkylidyne carbon resonance is found at 284 ppm and the CO resonances are found at 191.5 and 190.4 ppm. Inequivalence of the CO ligands and their similar chemical shifts suggest that one is trans to pyridine and the other is trans to chloride, as shown in eq 3. Carbonyl IR absorptions at 2075 and 1998 cm^{-1} are similar to those found in **3**.



(3)

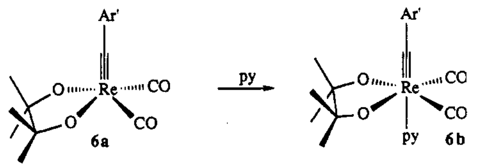
Addition of LiO-2,6-C_6H_3-*i*-Pr_2 (LiOAr) in THF to a slurry of **2** in dichloromethane causes **2** to dissolve rapidly as CO evolves and the solution becomes blood red. Re(CAr′)$(CO)_2(OAr)_2$(THF) (**5a**) can be isolated as ruby red crystals in 80% yield from a mixture of ether and pentane. Although 1 equiv of THF appears to be retained in the solid state, the NMR spectrum of **5a** in CD_2Cl_2 shows THF resonances that are identical to free THF. An NMR spectrum of a sample of **5a** in CD_2Cl_2 at −70 °C shows only broadening of the aryloxide isopropyl resonances and of the benzylidyne *o*-methyl resonances; the THF resonances are unchanged. Therefore we believe that in dichloromethane the THF is not bound to the metal to any significant extent. Two sets of two CO absorptions are observed in the solid state IR spectrum. A possible explanation is that THF is coordinated to the metal in the solid state to give two different octahedral isomers of **5a**.

Pyridine will react with **5a** to form a six-coordinate adduct (**5b**; eq 4) whose integrity is maintained in solution. Proton and carbon NMR data for **5b** are consistent with a structure in which one carbonyl ligand is trans to the pyridine ligand and the other trans to one of the aryloxides. The aryloxide ligands are inequivalent, and the isopropyl methyl groups are diastereotopic in each. If we assume that the carbonyl ligands are cis, the structure shown in eq 4 is a plausible one. The significant upfield shift of the alkylidyne carbon resonance in **5b** (284 ppm) compared to its chemical shift in **5a** (317 ppm) is noteworthy, and consistent with **5b** being six-coordinate in solution.



(4)

Addition of pinacol to **2** followed by triethylamine yields a cherry red solution from which yellow, pentane-soluble Re(CAr′)$(CO)_2(O_2C_2Me_4)$ (**6a**) can be isolated readily. The chemical shift of the alkylidyne ligand in **6a** is similar to its chemical shift in **5a**. Although **6a** shows no tendency to bind THF, it reacts quantitatively with pyridine to yield Re(CAr′)$(CO)_2(O_2C_2Me_4)$(py) (**6b**), which precipitates readily from benzene or ether. In NMR spectra of **6b** (CD_2Cl_2, 25 °C) the single pinacolate methyl group resonance is broad. At all temperatures below 10 °C, two sharp pinacolate methyl resonances are found. But not until the sample is cooled to −76 °C are sharp resonances for free and coordinated pyridine observed in the presence of excess pyridine; only two pinacolate methyl resonances are observed at −76 °C. At room temperature or below, the ^{13}C spectrum of **6b** shows a resonance for equivalent CO ligands and equivalent carbon atoms in the pinacolate ligand backbone. The benzylidyne resonance is observed at 300 ppm, upfield from where it is in five-coordinate **6a**. A plausible explanation is that pyridine binds in a position trans to the alkylidyne ligand to give a pseudo six-coordinate species, but it exchanges readily with free pyridine via the square pyramidal species, in which the pinacolate methyl groups exchange by a pseudorotation process at higher temperatures.



(5)

Addition of triphenylphosphine to **6a** results in rapid gas evolution and formation of dark red Re(CAr′)(CO)$(O_2C_2Me_4)(PPh_3)$ (**6c**). NMR data for **6c** are consistent with it being a nonfluxional complex in which the benzylidyne and phosphine ligands are in axial positions. (Two resonances are observed for the pinacolate methyl groups in proton and carbon NMR spectra, but only one resonance for the backbone carbon atoms.) The alkylidyne carbon resonance is found at 305.7 ppm in **6c** (J_{CP} = 15.6 Hz) and the carbonyl stretching frequency is found at 1953 cm^{-1}.

The syntheses reported here are relatively easy to perform and, except for **1**, proceed in high yield. As mentioned in the Introduction, mononuclear Re(V) alkylidyne complexes are relatively rare, and we could find no examples that contain alkoxide ligands. We also could find no other example of the use of triflic anhydride to remove "O^{2-}" from acyl ligands, although trifluoroacetic anhydride has been used for that purpose in several circumstances.[10] Triflic anhydride may prove to be a more powerful "O^{2-}" abstracting agent, and triflate complexes may be more versatile in subsequent reactions than halide or trifluoroacetate complexes. Unfortunately, attempts so far to oxidize the Re(V) complexes reported here to Re(VII), oxidations that on paper are analogous to those that yield d^0 trihalide alkylidyne complexes of Mo and W from d^2 complexes,[10] have failed. Nevertheless, we hope to eventually use this approach to synthesize Re(VII) alkylidyne complexes or to synthesize new Re(V) species that contain Re–carbon double or triple bonds.

Experimental Section

General Details. All manipulations were carried out under dinitrogen in a Vacuum/Atmospheres drybox, under argon using standard Schlenk techniques on a Schlenk line, or on a high-vacuum line. All solvents and liquid reagents were distilled under dinitrogen over sodium/benzophenone ketyl (THF, benzene, ether, pentane), molten sodium (toluene, pyridine) or CaH_2 (dichloromethane, NEt_3, phosphines), and stored over molecular sieves. Pentane was washed with 5% HNO_3/H_2SO_4 and dried over $CaCl_2$ prior to distillation, with tetraglyme added to dissolve the ketyl. THF was further purified by vacuum transfer from sodium/benzophenone ketyl under high vacuum just before use. $Re_2(CO)_{10}$ (Strem), triflic anhydride, tetraethylammonium chloride (Eastman), and 2,4,6-trimethylbenzoyl chloride (Lancaster) were purchased and used as received. Sodium metal was cut just prior to use and mercury (triply distilled, Aldrich) was filtered before use. All chemical shifts are reported in ppm downfield from TMS (^1H, ^{13}C) or H_3PO_4 (^{31}P, $P(OMe)_3$ external reference, δ 141 ppm). Deuterated solvents were stored over molecular sieves. Infrared spectra were recorded on a Perkin-Elmer 1400 spectrometer or a Mattson-Cygnus 100 FT-IR spectrometer as Nujol mulls between KBr plates. Microanalyses (C, H, N) were performed in our laboratory using a Perkin-Elmer PE2400 microanalyzer.

Preparation of Compounds. $Re[C(O)\text{-}2,4,6\text{-}C_6H_3Me_3](CO)_5$ (1). $Re_2(CO)_{10}$ (5.00 g, 7.66 mmol) was added to freshly prepared sodium amalgam (0.352 g Na, 15.3 mmol, 40 g Hg) in ether (85 mL) containing 4 mL of THF. The mixture was shaken vigorously for 5 min and allowed to stir overnight. This bright orange solution was decanted from the amalgam, filtered through Celite, and concentrated to a volume of 50 mL. 2,4,6-Trimethylbenzoyl chloride (2.59 mL, 15.3 mmol) was then added. After 1 h the mixture was filtered through Celite and the solvent was removed from the filtrate to afford an oil. The oil was extracted with pentane, the extract was filtered, and the pentane was removed in vacuo. The oil was dissolved in methylene chloride, the solution was passed through activated alumina, and the solvent was removed in vacuo. Recrystallization of the residue from pentane (three times) at -40 °C afforded 3.96 g (55%) of a pale yellow powder which was analytically pure: ^1H NMR δ 6.79 (s, 2, H_m), 2.27 (s, 6, Me_p), 2.19 (s, 3, Me_o); ^{13}C NMR δ 255.8 (ReC(O)), 183.5 (CO_{eq}), 181.9 (CO_{ax}), 157.9 (C_i), 136.3 (C_p), 129.1 (C_m), 127.2 (C_o), 21.0 (Me_p), 18.7 (Me_o). Anal. Calcd for $C_{15}H_{11}O_6Re$: C, 38.05; H, 2.34. Found: C, 37.72; H, 2.33.

$[Re(C\text{-}2,4,6\text{-}C_6H_3Me_3)(CO)_4(OTf)](OTf)$ (2). $Re[C(O)Ar'](CO)_5$ (3.325 g, 7.02 mmol) was dissolved in dichloromethane (85 mL) and the solution was chilled to −40 °C. Trifluoromethanesulfonic anhydride (1.182 mL, 7.02 mmol) was added while the solution was stirred rapidly. Large amounts of a white solid precipitated as gas evolved vigorously. The resulting slurry was filtered after 30 min, and the off-white solid was washed with toluene (2 × 20 mL) and pentane (4 × 20 mL) to afford analytically pure product (4.90 g, 96%): IR 2205 (w), 2140 (m) cm^{-1}. Anal. Calcd for $C_{16}H_{11}O_{10}S_2F_6Re$: C, 26.41; H, 1.52. Found: C, 26.36; H, 1.50.

$[NEt_4][Re(C\text{-}2,4,6\text{-}C_6H_3Me_3)(CO)_2Cl_3]$ (3). NEt_4Cl (1.05 g, 6.34 mmol) was added to a slurry of **2** (1.54 g, 2.11 mmol) in dichloromethane (40 mL) and the mixture was stirred for 4 h. The solution rapidly turned purple and then more slowly to pale lemon yellow. Gas evolved vigorously for a minute or two, followed by a slower loss over a 10–15 min period. Removing the solvent from this solution yielded an inseparable mixture of **3** and NEt_4OTf, but this mixture can be used in further reactions without purification: ^1H NMR (anion resonances only) δ 6.82 (s, 2, H_m), 2.60 (s, 6, Me_o), 2.24 (s, 3, Me_p); ^{13}C NMR δ 284.8 ($Re{\equiv}C$), 192.1 (CO), 144.8 (C_o), 144.7 (C_i), 141.1 (C_p), 128.7 (C_m), 21.9 (Me_p), 20.1 (Me_o); IR 2070 (s), 1978 (s) cm^{-1}.

$Re(C\text{-}2,4,6\text{-}C_6H_3Me_3)(CO)_2Cl_2(py)$ (4). Pyridine (1.71 mL, 2.11 mmol) and $TlBF_4$ (615 mg, 2.11 mmol) were added to the mixture containing **3** and Et_4NOTf described above. The solution was stirred overnight. The white precipitate was filtered off, and the filtrate was taken to dryness *in vacuo*. The residue was extracted with toluene. Concentration of the yellow solution gave 723 mg (65%) of pale yellow microcrystals. Recrystallization from a mixture of a minimum amount of dichloromethane and added ether at −40 °C afforded an analytically pure sample: ^1H NMR δ 9.20 (d, 2, py_o), 7.99 (t, 1, py_p), 7.51 (dd, 2, py_m), 6.90 (s, 2, H_m), 2.54 (s, 6, Me_o), 2.31 (s, 3, Me_p); ^{13}C NMR δ 284.1 ($Re{\equiv}C$), 191.5 (CO), 190.4 (CO), 154.5 (py_o), 146.4 (C_{aryl}), 146.2 (C_{aryl}), 140.4 (C_{aryl}), 140.1 (py_p), 129.3 (C_m), 126.2 (py_m), 22.2 (Me_p), 20.5 (Me_o); IR 2075 (s), 1998 (s) cm^{-1}. Anal. Calcd for $C_{17}H_{16}NO_2Cl_2Re$: C, 39.01; H, 3.08; N, 2.68. Found: C, 39.07; H, 3.19; N, 2.45.

$Re(C\text{-}2,4,6\text{-}C_6H_3Me_3)(CO)_2(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_2(THF)$ (5a). LiOAr etherate (2.29 g, 8.87 mmol) in THF (10 mL) was added to a rapidly stirred slurry of **2** (3.23 g, 4.44 mmol) in dichloromethane (60 mL) at −40 °C. The slurry dissolved to give a dark red solution, and CO evolved rapidly. After 1 h, the solvents were removed in vacuo and the residue was extracted with ether. The extract was filtered and crystallization induced by adding pentane and cooling the sample to −40 °C; yield 2.84 g (80%) of ruby red crystals: ^1H NMR δ 7.10 (d, 4, H_m), 6.96 (s, 2, H_m), 6.82 (t, 2, H_p), 3.48 (sept, 4, $CHMe_2$), 2.46 (s, 6, Me_o), 2.33 (s, 3, Me_p), 1.11 (d, 24, $CH\mathit{Me}_2$); ^1H NMR (−70 °C) δ 7.08 (d, 4, C_m), 6.89 (s, 2, C_m), 6.81 (t, 2, C_p), 3.42 (br s, 4, $CHMe_2$), 2.28 (br s, 6, Me_o), 2.25 (s, 3, Me_p), 1.17 (br s, 24, $CH\mathit{Me}_2$); ^{13}C NMR δ 316.8 ($Re{\equiv}C$), 197 (CO), 163 (C_i), 147 (C_i), 143 (C_o), 138 (C_o), 130 (C_p), 124 (C_m), 121 (C_p), 28.3 ($CHMe_2$), 24.7 ($CH\mathit{Me}_2$), 23.2 (Me_p), 20.2 (Me_o); IR (major) 2060 (s) and 1978 (vs) cm^{-1}; (minor) 2040 (m), 1944 (s) cm^{-1}. Anal. Calcd for $C_{40}H_{53}O_5Re$: C, 60.05; H, 6.68. Found: C, 59.69; H, 6.53.

$Re(C\text{-}2,4,6\text{-}C_6H_3Me_3)(CO)_2(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_2(py)$ (5b). Pyridine (15 μL, 190 μmol) was added to a toluene solution of **2** (105 mg, 125 μmol). The red solution turned yellow, and after 1 h the solvents were removed *in vacuo*. The residue was extracted with ether and crystallization induced in the filtered extract by adding pentane; yield 95 mg (95%): ^1H NMR (C_6D_6) δ 9.41 (d, 2, py_o), 7.32 (d, 2, H_m), 7.23 (d, 2, H_m), 7.04 (t, 1, H_p), 6.97 (t, 1, H_p), 6.87 (t, 1, py_p), 6.54 (dd, 2, py_m), 4.64 (sept, 2, $CHMe_2$), 3.33 (sept, 2, $CHMe_2$), 2.00 (s, 6, Me_o), 1.60 (s, 3, Me_p), 1.37 (d, 6, $CH\mathit{Me}_AMe_B$), 1.30 (d, 6, $CHMe_A\mathit{Me}_B$), 1.22 (d, 6, $CH\mathit{Me}_AMe_B$), 1.14 (d, 6, $CHMe_A\mathit{Me}_B$); ^{13}C NMR (C_6D_6) δ 284 ($Re{\equiv}C$), 194.7 (CO), 194.3 (CO), 165.6 (C_i), 160.7 (C_i), 153.2 (py_o), 143.5 (C_{aryl}), 142.6 (C_{aryl}), 142.2 (C_i), 139.3 (C_{aryl}), 138.9 (C_{aryl}), 129.0 (C_{aryl}), 126.1 (C_{aryl}), 122.7 (C_m), 118.9 (C_p), 116.8 (C_p), 26.7 ($CHMe_2$), 24.6 (Me_o), 23.8 & 23.7 ($CH\mathit{Me}_2$), 19.8 (Me_p); IR 2060 (m), 1988 (s) cm^{-1}.

$Re(C\text{-}2,4,6\text{-}C_6H_3Me_3)(CO)_2(O_2C_2Me_4)$ (6a). Pinacol (1.157 g, 9.796 mmol) was added to a rapidly stirred slurry of **2** (7.127 g, 9.796 mmol) in THF (45 mL). The slurry dissolved slowly over the period of 1 h to give a pale green solution. Addition of triethylamine (2.73 mL, 19.6 mmol) to the green solution resulted in an immediate color change to red. The solution was concentrated *in vacuo*. Celite was added to the two-phase mixture in order to assist removal of the oil (NEt_3HOTf) upon filtration of the mixture through more Celite. Concentration and repetition of this procedure affords a red solution to which pentane was added in order to induce crystallization of the product. The yellow product precipitated upon reducing the solution volume and cooling the mixture; yield 3.920 g (82%): ^{1}H NMR δ 6.88 (s, 2, H_m), 2.53 (s, 6, Me_o), 2.26 (s, 3, Me_p), 1.14 (s, 12, $O_2C_2Me_4$); ^{13}C NMR δ 317.8 ($Re\equiv C$), 201.4 (CO), 145 (C_{aryl}), 143.1 (C_i), 141.6 (C_{aryl}), 129.2 (C_m), 84.3 ($O_2\mathit{C}_2Me_4$), 28.2 ($O_2C_2\mathit{Me}_4$), 22.2 (Me_p), 20.7 (Me_o); IR 2060, 2047, 1979, 1960 cm^{-1}. Anal. Calcd for $C_{18}H_{23}O_4Re$: C, 44.16; H, 4.74. Found: C, 43.85; H, 4.94.

$Re(C\text{-}2,4,6\text{-}C_6H_3Me_3)(CO)_2(O_2C_2Me_4)(py)$ (6b). Pyridine (33 μL, 410 μmol) was added to an ether solution (7 mL) of **6a** (200 mg, 409 μmol). The red solution turned pale yellow within 30 s, and a large amount of a yellow precipitate appeared. After 15 min the solution was cooled to −40 °C, and 220 mg (95%) of a yellow powder was filtered off: ^{1}H NMR (25 °C) δ 8.63 (d, 2, py_o), 7.75 (t, 1, py_p), 7.34 (dd, 2, py_m), 6.82 (s, 2, H_m), 2.61 (s, 6, Me_o), 2.23 (s, 3, Me_p), 1.2 to −0.65 (v br, 12, $O_2C_2Me_4$); ^{1}H NMR (−76 °C) δ 8.60 (d, 2, py_o), 7.84 (t, 1, py_p), 7.42 (dd, 2, py_m), 6.78 (s, 2, H_m), 2.53 (s, 6, Me_o), 2.18 (s, 3, Me_p), 1.02 (s, 6, $O_2C\mathit{Me}_2CMe_2$), 0.46 (s, 6, $O_2CMe_2C\mathit{Me}_2$); ^{13}C NMR δ 299.9 ($Re\equiv C$), 200.9 (CO), 150.6 (py_o), 143.2 (C_i), 142.0 (C_p), 140.9 (C_o), 138.9 (py_p), 128.8 (C_m), 124.7 (py_m), 82.9 ($O_2\mathit{C}_2Me_4$), 27.9 ($O_2C_2\mathit{Me}_4$), 21.9 (Me_p), 20.3 (Me_o); ^{13}C NMR (−76 °C) δ 297.2 ($Re\equiv C$), 199.7 (CO), 149.6 (py_o), 142.2 (C_i), 141.3 (C_p), 140.1 (C_o), 138.7 (py_p), 128.0 (C_m), 124.9 (py_m), 81.4 ($O_2\mathit{C}_2Me_4$), 27.3 ($O_2C_2\mathit{Me}_2Me_2$), 26.5 ($O_2C_2Me_2\mathit{Me}_2$), 21.5 (Me_p), 19.8 (Me_o); IR 2033 (vs), 1956 (vs) cm^{-1}. Anal. Calcd for $C_{23}H_{28}NO_4Re$: C, 48.57; H, 4.96; N, 2.46. Found: C, 48.48; H, 5.23; N, 2.31.

$Re(C\text{-}2,4,6\text{-}C_6H_3Me_3)(CO)(O_2C_2Me_4)(PPh_3)$ (6c). Triphenylphosphine (109 mg, 417 μmol) was added to a rapidly stirred solution of **6a** (204 mg, 417 μmol) in ether (5 mL). The solution turned pale red and CO evolved vigorously. After 15 min the solution was concentrated *in vacuo*. Addition of 10 mL of pentane followed by 4 mL of ether resulted in dissolution of the resulting oil and subsequent precipitation of 226 mg (75%) of an orange-red powder within 2 min; the reaction appears to be quantitative by NMR: ^{1}H NMR δ 7.82 (m, 6, H_o), 7.38 (m, 3, H_p), 7.00 (m, 6, H_m), 6.44 (s, 2, H_m), 2.31 (s, 6, Me_o), 1.63 (s, 3, Me_p), 1.41 (s, 6, $O_2C_2\mathit{Me}_2Me'_2$), 1.27 (s, 6, $O_2C_2Me_2\mathit{Me}'_2$); ^{13}C NMR δ 305.7 (d, $J_{CP} = 15.6$ Hz, $Re\equiv C$), 219.4 (CO), 123.0 (C_{aryl}), 118.7 (C_{aryl}), 83.3 ($O_2\mathit{C}_2Me_4$), 28.3 ($O_2C_2\mathit{Me}_2Me'_2$), 27.6 ($O_2C_2Me_2\mathit{Me}'_2$), 22.7 ($CAr\text{-}o\text{-}\mathit{Me}_2$), 20.9 ($Me_p$); ^{31}P NMR δ 31.4 (s); IR 1953 cm^{-1}. Anal. Calcd for $C_{35}H_{38}O_3PRe$: C, 58.08; H, 5.29. Found: C, 58.19; H, 5.28.

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