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A Series of [3 + 2] Cycloaddition Products from the Reaction of Rhenium Oxo Complexes with Diphenyl Ketene

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The reaction of rhenium (VII) trioxo complexes containing the ligand sets scorpionate, $[HB(pz)_3]ReO_3$ (**6**), $[Ph–B(pz)_3]ReO_3$ (**7**), and $[\{HC(pz)_3\}ReO_3][ReO_4]$ (**8**) and pyridine/pyridine-type ligands [(4,7-diphenyl-1,10-phen)(Br)-ReO_3] (**12**), [(4,4′-di-*tert*-butyl-2,2′-dipyridyl)(Cl)ReO_3] (**13**), and $[(py)_2Re(Cl)O_3]$ (**4**), with diphenyl ketene, has led to the isolation of six novel [3 + 2] cycloaddition products. These air-stable solids **9**–**11** and **15**–**17** are the result of [3 + 2] addition of the O═Re═O motif across the ketene C═C double bond. Five of the six [3 + 2] cycloaddition products have been structurally characterized by single-crystal X-ray diffraction and in all cases by ^{13}C NMR and IR spectroscopies.

Introduction

As part of a research program aimed at defining unprecedented bond constructions and functional group transformations of organic molecules, we are investigating the activation of double bonds by transition metal oxides, beyond common cis-dihydroxylation using osmium tetroxide and permanganate. The osmium tetroxide catalyzed cis-dihydroxylation of alkenes is a very popular transformation[1] because of its wide substrate generality and protocols for enantioselective dihydroxylations that proceed with near complete stereoselectivity.[2] After some controversy,[3] the initial step of cis-dihydroxylation of C═C double bonds by osmium tetroxide is now accepted to proceed by a concerted [3 + 2] pathway with O═Os═O, after initial metal coordination of the olefin.[4]

The past few years have seen a large increase in the synthesis and use of rheniun oxo complexes,[5] highlighted by the use of methyltrioxo rhenium (MTO) as a highly efficient epoxidation catalyst.[6] The high reactivity of ketenes with organic substrates has led to increasing interest in their reactivity with metal complexes.[7] It has been shown that a ketene can react with metal oxo ligands across both the C═C and C═O bonds of the ketene.[8] Indeed, theoretical calculations suggest that altering the ligand set around rhenium oxo complexes may dictate the cyclization mode of this reaction.[9] Specifically, harder ligands such as O^- and

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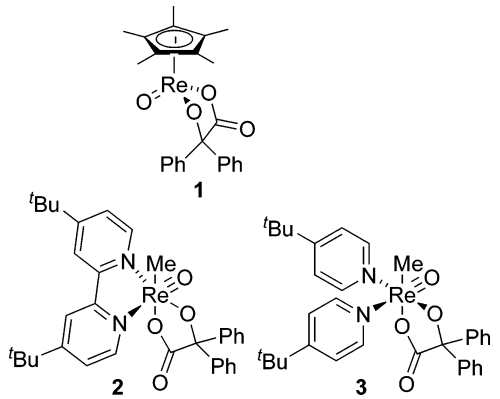

Figure 1. Products of rhenium oxo complexes with diphenyl ketene.

H_3PN favor the $[2 + 2]_{C=O}$ pathway, whereas the softer ligands (Cp and Me) prefer the $[2 + 2]_{C=C}$ pathway. The theoretical calculations revealed that the Cp ligands' ability to ring slip between η^5, η^3, and η^1 coordination modes was important in the ability of the complex to become coordinatively unsaturated. The [3 + 2] mode of addition is also competitive, but to our knowledge there have been only three previous examples of rhenium oxo complexes reacting with diphenyl ketene in this manner. It was shown by Herrmann et al. in 1985 that the stable mononuclear complex Cp^*ReO_3 can be reacted with an excess of diphenyl ketene in THF at room temperature to yield the corresponding [3 + 2] cycloaddition product (**1**) (Figure 1).[10] In 1994, Herrmann et al. also showed that when MTO was coordinated with a bipyridyl ligand, the resulting octahedral complex could be reacted with an excess of diphenyl ketene in THF to yield the corresponding [3 + 2] cycloaddition product (**2**).[11] It was also shown that when MTO·4-*tert*-butylpyridine was reacted with diphenyl ketene in the presence of an excess of 4-*tert*-butylpyridine base, an instantaneous [3 + 2] cycloaddition product (**3**) was formed (Figure 1).[11]

As theoretical calculations have shown that altering the ligand set around rhenium oxo complexes may alter the cyclization product formed,[9] we were interested to see if the use of alternative ligands on rhenium oxo complexes would alter the reactivity of the rhenium oxo complexes toward ketene. We have investigated two classes of ligands sets, scorpionates and pyridines, around a rhenium trioxo complex and have characterized their cycloaddition products with diphenyl ketene.

Experimental Section

Materials and Methods. All manipulations were performed under dry, oxygen-free nitrogen or argon using standard Schlenk techniques or in an Mbraun Unilab glovebox. THF was dried over and distilled from sodium benzophenone prior to use. Hexane was degassed and then dried by passing through a column of activated alumina. Diphenyl ketene was prepared by standard procedures.[12] The ligand $[Ph-B(pz)_3][H_2pz]$ was prepared according to a literature procedure.[13] Complexes $CpReO_3$ (**4**),[14] $[HB(pz)_3]ReO_3$ (**6**),[15] $[\{HC(pz)_3\}ReO_3][ReO_4]$ (**8**),[16] and [(4,4′-di-*tert*-butyl-2,2′-dipyridyl)(Cl)ReO_3] (**13**)[17] were prepared as described in the literature. All other reagents were obtained from commercial suppliers and used without further purification. NMR spectra were obtained on either a Brüker AMX400 or a Brüker AMX500 spectrometer. Mass spectra were acquired using VG micromass, 70E (EI), and AIMS 902 instruments. Elemental analysis was performed by the microanalysis service of the School of Chemistry, University of Nottingham, on an Exeter Analytical CE440 elemental analyzer. Melting points were obtained using a Reichert melting point apparatus. IR spectra were recorded as solids using an Avatar 320 FTIR spectrometer.

Compounds **9**, **10**, **11**, **14**, and **15** did not respond to mass spectral analysis in our hands by EI, CI, or FAB techniques. In addition, satisfactory elemental analyses were only obtained for compounds **12** and **16** despite multiple attempts. We have no satisfactory explanation for these compounds' noncompliance with our analytical techniques. In view of these facts, all ^1H and ^{13}C NMR spectra of the novel compounds in the experimental below are included in the Supporting Information as evidence of the bulk purity of these compounds by this technique.

$CpReOCl_2$ (5). To a stirred solution of $CpReO_3$ (**4**) (0.05 g, 0.17 mmol) in benzene (20 mL) was added $AlCl_3$ (0.04 g, 0.33 mmol). The suspension was heated to 50 °C and stirred for 12 h. The resulting suspension was filtered, and the solvent was removed in vacuo to afford an orange-brown solid, which was extracted into CH_2Cl_2. The resulting green solution was filtered and reduced in volume to ~5 mL. Cooling of the solution to −20 °C afforded $CpReOCl_2$ (**5**) as an air-stable green solid (0.02 g, 6.38 mmol, 38%): mp 150 °C (dec); IR υ_{max} (solid) 3095 (C−H), 1396, 970 (Re−O), 841; ^1H NMR (500 MHz, $CDCl_3$) δ_H 6.58 (5H, s, *Cp*); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 101.5 (Cp); *m*/*z* (EI+) 340 (51% M^+). Satisfactory elemental analysis unobtainable; see statement in Materials and Methods section above.

$[Ph-B(pz)_3]ReO_3$ (7). To a stirred suspension of Re_2O_7 (0.90 g, 1.86 mmol) in THF (30 mL) was added $[Ph-B(pz)_3][H_2pz]$ (2.00 g, 5.57 mmol), and the resulting pale blue-green solution was stirred at room temperature (rt) for 18 h. The solution was filtered, and the solvent was removed in vacuo to yield an oily green solid. Readdition of THF (5 mL) precipitated a white solid, which was filtered, washed with cold THF (15 mL), and dried in vacuo to afford $[Ph-B(pz)_3]ReO_3$ (**7**) as a white solid (0.44 g, 0.85 mmol, 46%): mp 210 °C (dec); IR υ_{max} (solid) 1407, 1301, 1210, 1079, 920 (Re−O), 779 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ_H 8.43 (3H, d, J = 2.2 Hz, Re−NC*H*), 7.92 (2H, m, *o*-Ph), 7.67 (3H, d, J = 2.5 Hz, B−NC*H*), 7.58 (3H, m, *m*/*p*-Ph), 6.35 (3H, t, J = 2.4 Hz, NCHC*H*); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 143.8, 136.2, 134.3, 129.4, 128.8, 106.5; *m*/*z* (EI+) 522 (M^+). Satisfactory elemental

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analysis unobtainable; see statement in Materials and Methods section above.

[HB(pz)$_3$]Re(═O)[η^2-O$_2$C(═O)─CPh$_2$] (9). To a stirred solution of diphenyl ketene (0.08 mL, 0.45 mmol) in CH_2Cl_2 (20 mL) was added **6** (0.10 g, 0.22 mmol). The suspension was stirred at rt for 18 h, filtered, and washed with CH_2Cl_2 (15 mL), and hexane was added until a mauve solid precipitated. The solid was filtered, washed with hexane (30 mL), and dried in vacuo to afford [HB(pz)$_3$]Re(═O)[η^2-O$_2$C(═O)─CPh$_2$] (**9**) as an air-stable mauve solid (0.06 g, 0.09 mmol, 41%). The product was recrystallized to afford mauve crystals suitable for X-ray diffraction by cooling via a CH_2Cl_2/hexane solution: mp 132−135 °C; IR υ_{max} (solid) 3120, 1707 (CO), 1407, 1213, 1052, 982 (Re−O), 774 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$), * denotes ligand trans to Re═O, δ_H 7.95 (1H, d, J = 2.4 Hz, Re−NC*H*), 7.94 (1H, d, J = 2.2 Hz, B−NC*H*), 7.89 (1H, d, J = 2.1 Hz, Re−NC*H*), 7.77−7.75 (3H, m, B−NC*H* + 2Ph), 7.44 (1H, d, J = 1.4 Hz, *o*-Ph), 7.43 (1H, d, J = 1.0 Hz, *o*-Ph), 7.26−7.12 (8H, m, Re−NC*H** + 7Ph), 6.92 (1H, d, J = 2.1 Hz, B−NC*H**), 6.45 (1H, t, J = 2.4 Hz, NCHC*H*), 6.32 (1H, t, J = 2.3 Hz, NCHC*H*), 5.70 (1H, t, J = 2.3 Hz, NCHC*H**); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 184.1 (*C*═O), 147.9, 143.5, 142.9, 140.1, 138.2, 134.6, 128.9−126.7 (10C, m, Ph), 108.7, 108.0, 105.4, 94.2 (*C*Ph$_2$). Structure confirmed by X-ray crystallography; satisfactory elemental analysis and *m*/*z* unobtainable; see statement in Materials and Methods section above.

[Ph−B(pz)$_3$]Re(═O)[η^2-O$_2$C(═O)─CPh$_2$] (10). To a stirred solution of diphenyl ketene (0.07 mL, 0.38 mmol) in THF (20 mL) was added complex **7** (0.10 g, 0.19 mmol). The suspension was stirred at rt for 18 h, filtered, and washed with THF (3 × 5 mL). Hexane was added until a blue solid precipitated. The precipitate was filtered, washed with hexane, and dried in vacuo to afford [Ph−B(pz)$_3$]Re(═O)[η^2-O$_2$C(═O)─CPh$_2$] (**10**) as an air-stable blue solid (0.05 g, 0.08 mmol, 41%). The product was recrystallized to afford blue crystals suitable for X-ray diffraction by cooling in a CH_2Cl_2 solution to −20 °C overnight: mp 180 °C (dec); IR υ_{max} (solid) 1705 (CO), 1406, 1300, 1171, 1071, 976 (Re−O), 889, 789 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) * denotes ligand trans to Re═O, δ_H 8.16 (1H, d, J = 2.3 Hz, Re−NC*H*), 8.09 (1H, d, J = 2.8 Hz, Re−NC*H*), 8.00 (1H, d, J = 2.4 Hz, *o*-Ph), 7.98 (1H, t, J = 1.6 Hz, *p*-Ph), 7.92 (1H, d, J = 1.4 Hz, *o*-Ph), 7.90 (1H, t, J = 0.9 Hz, *p*-Ph), 7.78 (1H, d, J = 2.4 Hz, Re−NC*H**), 7.75 (1H, d, J = 2.6 Hz, B−NC*H*), 7.63−7.56 (5H, m, Ph), 7.50 (1H, d, J = 2.6 Hz, B−NC*H*), 7.40−7.33 (4H, m, Ph), 7.30−7.25 (2H, m, Ph), 7.09 (1H, d, J = 2.2 Hz, B−NC*H**), 6.47 (1H, t, J = 2.4 Hz, NCHC*H*), 6.39 (1H, t, J = 2.3 Hz, NCHC*H*), 5.85 (1H, t, J = 2.3 Hz, NCHC*H**); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 184.3 (*C*═O), 149.6, 148.6, 143.8, 143.6, 143.5, 141.6, 139.2, 134.5, 134.1, 129.4, 128.9, 128.7, 128.7, 128.3, 127.9, 127.6, 127.4, 127.2, 126.8, 108.4, 107.9, 105.3, 94.0 (*C*Ph$_2$). Structure confirmed by X-ray crystallography; satisfactory elemental analysis and *m*/*z* unobtainable; see statement in Materials and Methods section above.

{[HC(pz)$_3$]Re(═O)[η^2-O$_2$C(═O)─CPh$_2$]}{ReO$_4$} (11). To a stirred solution of diphenyl ketene (0.05 mL, 0.29 mmol) in CH_2Cl_2 (20 mL) was added **8** (0.10 g, 0.14 mmol). The suspension was stirred at rt for 18 h, filtered, and washed with CH_2Cl_2 (3 × 5 mL), and hexane was added until a purple solid precipitated. The precipitate was filtered in air, washed with hexane, and dried in vacuo to afford [HC(pz)$_3$Re(═O)(η^2-O$_2$C(═O)─CPh$_2$)][ReO$_4$] (**11**) as an air-stable purple solid (0.10 g, 0.11 mmol, 78%). The product was recrystallized to afford purple crystals suitable for X-ray diffraction by cooling in a CH_2Cl_2 solution to −20 °C overnight: mp 156−159 °C; IR υ_{max} (solid) 1727 (C═O), 1409, 1285, 1170, 985 (Re−O), 916 (Re−O), 778 cm^{-1}; ^{1}H NMR (500 MHz, CD_3CN) * denotes ligand trans to Re═O, δ_H 9.22 (1H, s, C*H*), 8.76 (1H, d, J = 2.1 Hz, Re−NC*H*), 8.60 (1H, d, J = 2.8 Hz, Re−NC*H*), 8.43 (1H, d, J = 2.3 Hz, C−NC*H*), 8.32 (1H, d, J = 2.1 Hz, C−NC*H*), 8.11 (1H, d, J = 2.6 Hz, Re−NC*H**), 7.79−7.74 (2H, m, Ph), 7.54−7.50 (2H, m, Ph), 7.44−7.30 (6H, m, Ph), 7.13 (1H, d, J = 2.0 Hz, C−NC*H**), 6.96 (1H, t, J = 2.7 Hz, NCHC*H*), 6.81 (1H, t, J = 2.6 Hz, NCHC*H*), 6.18 (1H, t, J = 2.5 Hz, NCHC*H**); ^{13}C NMR (125 MHz, CD_3CN) δ_C 182.9 (*C*═O), 152.4, 152.1, 145.9, 143.5, 143.5, 141.8, 139.9, 135.8, 129.5, 129.2, 129.1, 128.9, 127.5, 127.1, 112.0, 111.4, 109.1, 94.1 (*C*Ph$_2$). Structure confirmed by X-ray crystallography; satisfactory elemental analysis and *m*/*z* unobtainable; see statement in Materials and Methods section above.

[(4,7-Diphenyl-1,10-phen)ReO$_3$Br] (12). To a suspension of NH_4ReO_4 (0.27 g, 1.00 mmol) in HBr (5 mL) was added a solution of 4,7-diphenyl-1,10-phenathroline (0.66 g, 2.00 mmol) in AcOH (15 mL). The yellow suspension turned to a clear yellow solution within 15 min. After 1 h a yellow solid had precipitated. The suspension was stirred for another 4 h, after which time the precipitate was filtered, washed with EtOH/cold Et_2O, and dried in vacuo to afford [(4,7-diphenyl-1,10-phen)ReO$_3$Br] (**12**) as an air-stable yellow solid (0.29 g, 0.44 mmol, 44%): mp 240 °C (dec); IR υ_{max} (solid) 3399 (C−H), 1623, 1603, 1430, 1237, 941 (Re−O), 898 (Re−O), 854, 769 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 9.50 (2H, d, J = 5.3 Hz, Re−NC*H*), 8.17 (2H, s, NCCC*H*), 8.03 (2H, d, J = 5.3 Hz, NCHC*H*), 7.66−7.58 (10H, m, *Ph*); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 153.6, 151.1, 142.2, 135.3, 130.4, 129.7, 129.5, 129.0, 126.5, 125.9; *m*/*z* (EI+) 332 (100% M$^+$ − ReO$_3$Br). Anal. Calcd For $C_{24}H_{16}BrN_3O_3Re$: C, 44.59; H, 2.49; N, 4.33. Found C, 45.19; H, 2.43; N, 4.29.

[(py)$_2$Re(Cl)O$_3$] (14). To a stirred suspension of Re_2O_7 (0.30 g, 0.62 mmol) in THF (10 mL) was added trimethylsilyl chloride (0.16 mL, 1.24 mmol), and the resulting pale yellow solution was stirred at rt for 10 min. To the solution was added pyridine (0.11 mL, 1.30 mmol), resulting in the immediate precipitation of a pale green solid. The suspension was stirred at rt for a further 30 min, and the solvent was removed via filter cannula. The solid was washed with THF and dried in vacuo to afford [(py)$_2$Re(Cl)O$_3$] (**14**) as an air-sensitive pale green solid (0.22 g, 0.52 mmol, 40%): mp 190−192 °C; IR υ_{max} (solid) 1607, 1536, 1488, 902 (Re−O) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 8.95 (4H, d, J = 5.0 Hz, *o*-py), 8.01 (2H, tt, J = 7.7 Hz, 1.6, *p*-py), 7.52 (4H, t, J = 6.5 Hz, *m*-py); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 150.3, 140.4, 125.5. Satisfactory elemental analysis and *m*/*z* unobtainable; see statement in Materials and Methods section above.

[(4,7-Diphenyl-1,10-phen)(Br)Re(═O)(η^2-O$_2$C(═O)─CPh$_2$)] (15). To a stirred solution of diphenyl ketene (0.06 mL, 0.37 mmol) in CH_2Cl_2 (20 mL) was added complex **12** (0.12 g, 0.19 mmol). The solution was stirred at rt for 6 h. Hexane was added until an orange solid precipitated. The product was filtered in air, washed with CH_2Cl_2/hexane, and dried in vacuo to afford [(4,7-diphenyl-1,10-phen)(Br)Re(═O)(η^2-O$_2$C(═O)─CPh$_2$)] (**15**) as an air-stable orange solid (0.13 g, 0.15 mmol, 81%). Crystals suitable for X-ray diffraction were obtained from slow evaporation of a THF solution: mp 183−185 °C (dec); IR υ_{max} (solid) 3039 (C−H), 1714 (C═O), 1233, 1173, 975 (Re−O), 832, 766 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) * denotes ligand trans to Re═O, δ_H 9.45 (1H, d, J = 5.7 Hz, Re−NC*H*), 8.33 (1H, d, J = 5.4 Hz, Re−NC*H**), 8.09 (1H, d, J = 9.5 Hz, Ar), 8.01−7.97 (2H, m, NCHC*H* + Ar), 7.88 (2H, d, J = 8.1 Hz, Ar), 7.67 (2H, t, J = 7.8 Hz, Ar), 7.61−7.56 (6H, m, Ar), 7.51 (2H, d, J = 8.0 Hz, Ar), 7.46−7.42 (4H, m, Ar), 7.38 (3H, t, J = 7.2 Hz, Ar), 7.29 (1H, d, J = 7.5, Ar), 7.14 (1H, d, J = 5.4 Hz, NCHC*H**); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 181.7

Table 1. Crystal Data and Summary of Data Collection and Structure Refinement

	9	10	11	15	17
chem formula	$C_{23}H_{20}BN_4O_3Re\cdot 0.63(C_4H_8O)$	$C_{33}H_{32}BN_2O_5Re$	$C_{24}H_{19}N_6O_2Re\cdot ReO_4\cdot CH_2Cl_2\cdot 0.25(CH_4O)$	$C_{38}H_{26}BrN_2O_4Re\cdot C_2H_8O$	$C_{24}H_{20}ClNO_4Re\cdot CH_2Cl_2$
M_r	686.53	789.66	984.79	912.82	707.00
cryst syst	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	15.1042 (10)	8.4662 (7)	8.5255 (4)	13.1274 (8)	14.402 (2)
b (Å)	8.3461 (6)	11.2918 (10)	31.2728 (14)	19.7989 (12)	16.830 (3)
c (Å)	21.8796 (14)	17.789 (2)	12.1317 (6)	13.8541 (8)	21.932 (3)
α (deg)	90	72.523 (1)	90	90	90
β (deg)	90.758 (2)	78.082 (1)	104.291 (2)	99.550 (2)	108.140 (3)
γ (deg)	90	72.196 (1)	90	90	90
V (Å^3)	2757.9 (5)	1532.0 (4)	3134.4 (3)	3550.9 (6)	5052 (2)
Z	4	2	4	4	8
D (Mg m^{-3})	1.653	1.712	2.087	1.707	1.859
radiation type	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα
μ (mm^{-1})	4.45	4.02	7.94	4.60	5.16
T (K)	150(2)	150(2)	150(2)	150(2)	150(2)
$R[F \geq 4\sigma(F)]$	0.030	0.034	0.031	0.027	0.035
$R_w(F^2)$	0.070	0.079	0.082	0.068	0.060
S	1.07	1.10	1.01	0.98	0.81

(*C*═O), 155.4, 151.2, 150.9, 148.5, 146.3, 143.8, 142.0, 141.3, 140.8, 135.1, 133.7, 131.1, 130.3, 130.1, 129.6, 129.3, 128.6, 128.5, 128.4, 128.1, 127.7, 126.4, 126.3, 125.2, 124.7, 122.8, 98.1 (*C*Ph$_2$). Structure confirmed by X-ray crystallography; satisfactory elemental analysis and *m*/*z* unobtainable; see statement in Materials and Methods section above.

[(4,4′-Di-*tert*-butyl-2,2′-dipyridyl)(Cl)Re(═O)][η^2-O$_2$C(═O)—CPh$_2$] (16). To a stirred solution of diphenyl ketene (0.13 mL, 0.74 mmol) in CH_2Cl_2 (20 mL) was added complex **13** (0.20 g, 0.37 mmol). The solution was stirred at rt for 18 h, after which time the suspension was filtered and washed with more CH_2Cl_2 and hexane was added until a green solid precipitated. The solid was isolated by filtration, washed with hexane, and dried in vacuo to afford [(4,4′-di-*tert*-butyl-2,2′-dipyridyl)(Cl)Re(═O)][η^2-O$_2$C(═O)—CPh$_2$] (**16**) as an air-stable green solid (0.18 g, 0.25 mmol, 68%): mp 244−246 °C; IR υ_{max} (solid) 2968 (C−H), 1710 (C═O), 1617, 1415, 1230, 1173, 974 (Re−O), 835 (Re−O), 774 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) * denotes ligand trans to Re═O, δ_H 9.14 (1H, d, J = 6.3 Hz, NC*H*), 8.21 (1H, s, NCC*H*), 7.93 (1H, d, J = 6.0 Hz, NC*H**), 7.89 (1H, s, NCC*H**), 7.80 (2H, dd, J = 7.8 Hz, 1.2, *m*-Ph), 7.67 (1H, dd, J = 6.3 Hz, 2.0, NCHC*H*), 7.52 (2H, d, J = 8.4, *o*-Ph), 7.42−7.31 (5H, m, Ph), 7.24 (1H, t, J = 7.1 Hz, *p*-Ph), 6.80 (1H, d, J = 6.1 Hz, NCHC*H**), 1.47 (9H, s, C*H*$_3$), 1.34 (9H, s, C*H*$_3$*); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 182.4 (*C*═O), 168.4, 165.1, 154.5, 151.6, 149.0, 148.2, 143.6, 142.9, 128.3, 128.0, 127.9, 127.6, 126.4, 123.4, 121.6, 118.6, 117.0, 97.6 (*C*Ph$_2$), 35.6 (*C*(CH$_3$)$_3$), 34.5 (*C**(CH$_3$)$_3$), 31.5 (*C*H$_3$), 30.4 (*C*H$_3$*); *m*/*z* (FAB) 732 (64% M$^+$). Anal. Calcd For $C_{32}H_{34}ClN_2O_4Re$: C, 52.45; H, 4.68; N, 3.83. Found C, 52.13; H, 4.54; N, 3.83.

[(py)$_2$(Cl)Re(═O)][η^2-O$_2$C(═O)—CPh$_2$] (17). To a stirred solution of diphenyl ketene (0.08 mL, 0.47 mmol) in CH_2Cl_2 (20 mL) was added **14** (0.10 g, 0.23 mmol). The suspension was stirred at rt for 18 h, after which time the suspension was filtered and washed with more CH_2Cl_2 and hexane was added until a blue solid precipitated. The precipitate was filtered, washed with hexane, and dried in vacuo to afford [(py)$_2$(Cl)Re(═O)][η^2-O$_2$C(═O)—CPh$_2$] (**17**) as an air-stable bright blue solid (0.12 g, 0.19 mmol, 80%). Crystals suitable for X-ray diffraction were obtained by slow evaporation of a CH_2Cl_2 solution: mp 188−192 °C; IR υ_{max} (solid) 1673 (C═O), 1454, 1297, 956 (Re−O), 780, 764 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 8.95 (4H, d, J = 6.2 Hz, *o*-py), 7.68 (2H, t, J = 7.7 Hz, *p*-py), 7.52 (4H, t, J = 6.6 Hz, *m*-py), 7.02 (6H, d, J = 7.3 Hz, *o*/*m*-Ph), 6.95 (4H, t, J = 7.1 Hz, *p*-Ph); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 174.6 (*C*═O), 153.9 (py), 142.7 (py), 141.6 (py), 127.6 (Ph), 127.0 (Ph), 126.3 (Ph), 124.6 (Ph), 95.0 (*C*Ph$_2$); *m*/*z* (ES) 621 (41% M$^+$ + H). Structure confirmed by X-ray crystallography; satisfactory elemental analysis unobtainable; see statement in Materials and Methods section above.

X-ray Crystallography. All single-crystal diffraction data were collected using graphite-monochromated Mo Kα X-radiation on SMART APEX or SMART1000 CCD area detector diffractometers equipped with Oxford Cryosystems open-flow cryostats.[18] All data were collected at 150(2) K. Details of the individual data collections and refinements are given in Table 1. All structures were solved by direct methods using SHELXS97[19] or SIR92[20] and were then developed and refined by full-matrix least-squares refinement against F^2 using SHELXL97.[21] All fully occupied non-H atoms were refined with anisotropic atomic displacement parameters. Hydrogen atoms were placed geometrically and thereafter refined as part of a riding model.

In **9**, the lattice contains diffuse solvent and PLATON SQUEEZE[22] identified 2.5 molecules of THF per unit cell. These are included in the cell contents and in the calculation of formula weight, density, etc., but their contribution to the diffraction pattern was removed. Disorder of the phenyl ring was modeled by two half-occupied orientations, with geometric restraints applied to the ring geometry and the atoms refining with isotropic displacement parameters.

In **11**, one solvent region was poorly defined and PLATON SQUEEZE[22] revealed a void volume of 312 Å^3 and 17 electrons per unit cell. This electron density was interpreted as one MeOH per unit cell; this is included in the unit cell contents and in the calculation of the formula, formula weight, density, etc. but does not contribute to the diffraction pattern.

Results and Discussion

The rhenium trioxo complex Cp*ReO$_3$ reacts with diphenyl ketene to give a [3 + 2] cycloaddition product **1** (Figure 1).[10] We were interested to see if the Cp analogue, CpReO$_3$ (**4**),[17] would react with diphenyl ketene to give an alternate

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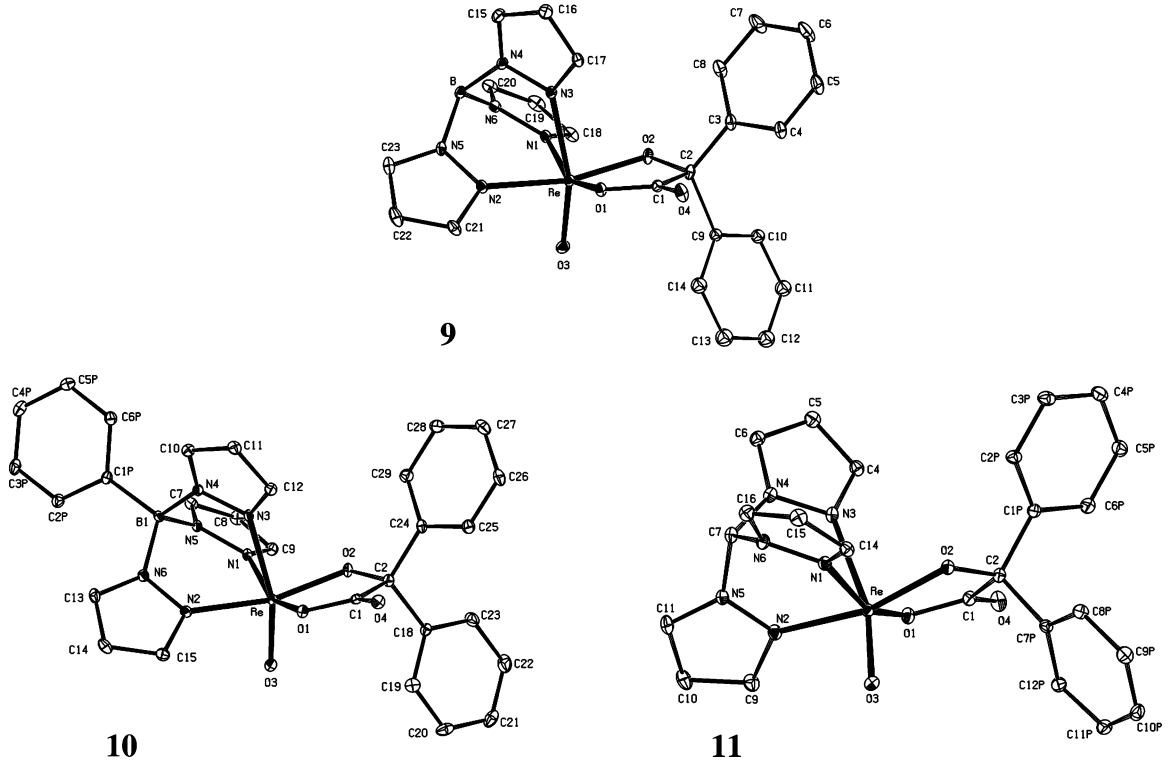

Figure 2. X-ray crystal structure of complexes **9**, **10**, and **11**.

cycloaddition product. Therefore $CpReO_3$ was synthesized and reacted with diphenyl ketene under a variety of alternate conditions, but we could not isolate any cycloaddition products from the reaction of $CpReO_3$ with diphenyl ketene. Reaction of $CpReO_3$ with $AlCl_3$ yielded the air-stable complex $CpReOCl_2$ (**5**) as a green crystalline solid in 38% yield. The ^1H and ^{13}C NMR spectra of complex **5** both showed singlet resonances, indicating that the Cp ring was η^5 coordinated, as in $CpReO_3$. Despite the addition of more electronegative Cl ligands, the singlet resonance in the ^1H NMR spectrum for the Cp ring in **5** (δ 6.58) lay upfield of the Cp resonance for $CpReO_3$ (**4**, δ 6.93). We attribute this to the remaining oxo ligand of **5** acting as a 6-electron donor to the rhenium metal, ensuring an 18-electron complex. Thus the increase in electron density on the rhenium metal results in increased shielding of the Cp protons. Unfortunately, upon reaction of $CpReOCl_2$ (**5**) with diphenyl ketene, no cyclization products were detected.

In trying to mimic the Cp system, but provide a ligand which may be able to partially dissociate to reveal an additional coordination site, we chose to study the reactivity of rhenium oxo complexes containing tris(pyrazolyl) "scorpionate" ligands. These facially coordinating, negatively charged, six-electron donating ligands are often compared electronically to cyclopentadienyl ligands.[23]

The known scorpionate complex $[HB(pz)_3]ReO_3$ (**6**)[14] (where pz = pyrazole), its more soluble congener $[Ph-B(pz)_3]ReO_3$ (**7**),[24] and the more electropositive $[\{HC(pz)_3\}ReO_3][ReO_4]$ (**8**)[15] were prepared. The literature showed only one synthesis of $[Ph-B(pz)_3]ReO_3$ (**7**)[24] from the reaction of Re_2O_7 with $[Ph-B(pz)_3]Na$.[25] We found the synthesis of $[Ph-B(pz)_3]Na$ to be difficult and instead synthesized $[Ph-B(pz)_3]ReO_3$ (**7**) from the reaction of Re_2O_7 with $[Ph-B(pz)_3][H_2pz]$ (where H_2pz is protonated pyrazole) as the scorpionate ligand source. Treatment of **6**−**8** with diphenyl ketene gave the novel complexes $[HB(pz)_3]Re(=O)[\eta^2\text{-}O_2C(=O)-CPh_2]$ (**9**), $[Ph-B(pz)_3]Re(=O)[\eta^2\text{-}O_2C(=O)-CPh_2]$ (**10**), and $[\{HC(pz)_3\}Re(=O)\{\eta^2\text{-}O_2C(=O)-CPh_2\}][ReO_4]$ (**11**) as air-stable blue-purple solids in 41, 41, and 78% yields, respectively. The ^{13}C NMR spectra of **9**−**11** were in strong agreement with those of the three previously published rhenium−ketene [3 + 2] cycloaddition products **1**−**3** (Figure 1)[10,11] in that the *C*O carbon of diphenyl ketene shifted upfield, whreas the *C*Ph_2 carbon was downfield of diphenyl ketene (Table 2). The IR spectra of the complexes were also in strong agreement with those of complexes **1**−**3** (Figure 1). Interestingly, the carbonyl resonance for **11** was ∼20 cm^{-1} higher than those of the other scorpionate complex [3 + 2] cycloaddition products **9** and **10** (1727 versus ∼1705 cm^{-1}, Table 2). This could be justified, as both cycloaddition products **9** and **10** contained an overall negatively charged scorpionate ligand, resulting in an increase in donation of electron density to the metal compared to that in **11**.

Crystals suitable for single-crystal X-ray diffraction were obtained by cooling CH_2Cl_2 solutions to −20 °C. The X-ray structures (Figure 2) revealed a distorted octahedral arrangement around the central rhenium atom, with all three pyrazole rings coordinated to the central rhenium metal. Complex **11**

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Table 2. Selected Spectral Data for Compounds **9**−**11**

	9	**10**	**11**
$\nu_{C=O}/cm^{-1}$	1707	1705	1727
ν_{Re-O}/cm^{-1}	982	976	985
^{13}C NMR *C*O/ppm	184.1	184.3	182.9
^{13}C NMR *C*Ph_2/ppm	94.2	94.0	94.1

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **9**, **10**, and **11**

	9	**10**	**11**
Re−O(1)	1.997(3)	2.008(3)	1.967(3)
Re−O(2)	1.938(3)	1.933(3)	1.924(3)
Re−O(3)	1.671(3)	1.688(3)	1.677(3)
Re−N(1)	2.066(3)	2.050(3)	2.074(3)
Re−N(2)	2.120(3)	2.130(3)	2.119(4)
Re−N(3)	2.242(3)	2.256(3)	2.292(4)
O(1)−Re−O(2)	81.04(12)	80.98(11)	81.12(12)
O(1)−Re−O(3)	106.08(13)	104.55(13)	108.56(15)
O(1)−Re−N(1)	156.18(12)	156.76(12)	154.80(14)
O(1)−Re−N(2)	94.81(12)	95.56(12)	93.04(13)
O(1)−Re−N(3)	80.28(11)	80.55(12)	80.73(13)
O(2)−Re−O(3)	106.86(14)	107.60(13)	106.83(15)
O(2)−Re−N(1)	88.04(12)	88.54(12)	89.82(12)
O(2)−Re−N(2)	165.72(12)	165.16(12)	162.99(14)
O(2)−Re−N(3)	88.46(12)	87.95(12)	87.44(12)
O(3)−Re−N(1)	97.31(14)	98.37(14)	96.55(15)
O(3)−Re−N(2)	87.41(14)	87.24(13)	90.16(16)
O(3)−Re−N(3)	164.02(13)	164.12(13)	163.79(14)
N(1)−Re−N(2)	90.60(12)	89.28(13)	88.86(14)
N(1)−Re−N(3)	78.31(12)	78.39(13)	75.39(13)
N(2)−Re−N(3)	77.35(12)	77.24(12)	75.83(14)

was still positively charged overall, shown by the presence of the $[ReO_4]^-$ counterion. The cyclization products **9**−**11** resulted from a net [3 + 2] cycloaddition of the C═C double bond of diphenyl ketene across a O═Re═O unit of the scorpionate complex and to our knowledge are the first isolated examples of a scorpionate complex cycloaddition with a ketene. The two Re−O bonds of the five-membered metallocycles are of similar length to those of the previously reported scorpionate-containing rhenium (V) oxo complexes.[26] (Table 3). The development of triple bond character in the Re−oxo ligand bond could be seen from the X-ray crystal structures, where the Re−O(3) bond length was shorter than any of the three Re−O double bonds in the starting material $HB(pz)_3ReO_3$ (**6**) (1.708(2), 1.707(2), and 1.720(2) Å).[14] This results in an extension of the trans Re−N(3) bond length compared with the other two Re−N bond lengths of the coordinated pyrazole rings.

Having isolated three [3 + 2] cycloaddition products from the reaction of scorpionate complexes with diphenyl ketene, we turned to other ligand systems that could potentially disassociate during the reaction between rhenium trioxo complexes and diphenyl ketene to see if they could have an influence upon the cyclization mode of the addition complexes. It had been shown previously that MTO does not react with diphenyl ketene unless precoordination of pyridine-type ligands takes place, to ultimately produce complexes **2** and **3**.[11] The chloro analogue of MTO (i.e., Cl−ReO_3) is known, and it was hoped that the electron-withdrawing effect of the chloro group would increase the

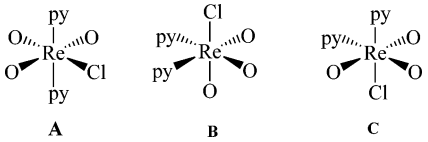

Figure 3. Possible coordination geometries for complex **14**.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **15** and **17**

	15	**17**
Re−O(1)	1.987(2)	2.091(3)
Re−O(2)	1.922(2)	1.923(3)
Re−O(3)	1.683(2)	1.683(3)
Re−N(1)	2.238(2)	2.122(4)
Re−N(2)	2.144(3)	2.136(4)
Re−X	2.5295(4)[a]	2.3454(12)[b]
O(1)−Re−O(2)	81.14(9)	76.38(13)
O(1)−Re−O(3)	103.89(10)	87.68(14)
O(1)−Re−N(1)	83.24(8)	89.28(14)
O(1)−Re−N(2)	88.66(9)	87.09(13)
O(1)−Re−X	160.32(6)[a]	169.33(9)[b]
O(2)−Re−O(3)	111.07(10)	164.00(14)
O(2)−Re−N(1)	88.70(9)	86.15(14)
O(2)−Re−N(2)	159.91(9)	88.39(14)
O(2)−Re−X	87.35(6)[a]	92.95(9)[b]
O(3)−Re−N(1)	159.66(10)	92.46(15)
O(3)−Re−N(2)	88.11(10)	92.13(15)
O(3)−Re−X	95.11(8)[a]	102.98(12)[b]

[a] X = Br. [b] X = Cl.

electrophilicity of the central rhenium metal ion toward the alkene of ketene. There was also the potential that the chloro ligand could act as a spectator ligand and stabilize transition states or intermediates during the cycloaddition reaction.[27] Therefore, Cl−ReO_3 was made in situ from the reaction of Re_2O_7 with trimethylsilyl chloride,[17]and after 10 min diphenyl ketene was added to the reaction. The pale yellow THF solution immediately turned bright purple, but ^{13}C NMR revealed that a complex mixture of products was formed, none of which could be isolated.

We therefore synthesized the known trioxo complex [(1,-10-phen)ReO_3Br][28] but unfortunately encountered problems with the solubility of this complex in most common organic solvents. Synthesis of the novel complex [(4,7-diphenyl-1,-10-phen)ReO_3Br] (**12**) by a similar procedure gave a more soluble complex in 41% yield. For comparison purposes, the known rhenium trioxo complex [(4,4′-di-*tert*-butyl-2,2′-dipyridyl)ReO_3Cl] (**13**)[17] was also prepared. In an attempt to aid possible ligand dissociation as a preliminary step for an alternative cyclization mode, we decided to synthesize the analogous and more labile pyridine complex. We synthesized Cl−ReO_3 in situ as above and added an excess of pyridine. A pale green, air-sensitive solid immediately precipitated out of solution and was isolated as the novel rhenium trioxo complex [$(py)_2ReO_3Cl$] (**14**) in 40% yield. Assuming that there is no rapid pyridine ligand site exchange, of which we detected no evidence, the precise structure of complex **14** could have been one of three possibilities (Figure 3). The $^1H/^{13}C$ NMR spectra showed a single pyridine resonance, ruling out the possibility of structure **C**, although

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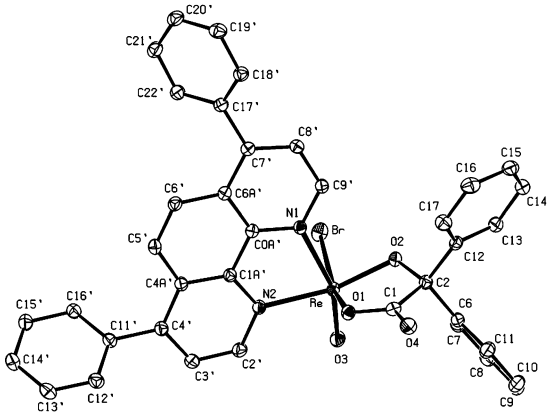
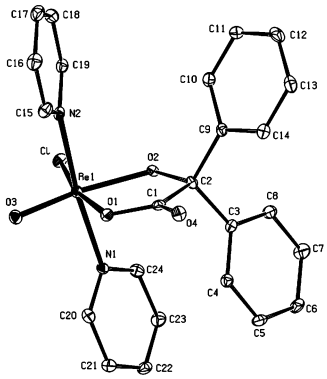


15



17

Figure 4. X-ray crystal structure of [3 + 2] cycloaddition products **15** and **17**.

it could not be determined at this stage whether the pyridine ligands were cis (**A**) or trans (**B**).

Treatment of complexes **12**−**14** with excess diphenyl ketene in CH_2Cl_2 at room temperature gave the novel complexes [(4,7-diphenyl-1,10-phen)(Br)Re(═O)(η^2-O_2C(═O)−CPh_2)] (**15**), [(4,4′-di-*tert*-butyl-2,2′-dipyridyl)(Cl)Re(═O)][η^2-O_2C(═O)−CPh_2] (**16**), and [(py)$_2$(Cl)Re(═O)][η^2-O_2C(═O)−CPh_2] (**17**) as air-stable solids in 81, 68, and 80% yields, respectively. Crystals suitable for X-ray structure determination could only be obtained for products **15** and **17**. Like that of the previously reported [3 + 2] cycloaddition product **2**,[11] the single-crystal X-ray diffraction structure of (**15**) showed that a single isomer of the product was formed (Figure 4, Table 4). The geometry around the metal is a distorted octahedron (Figure 4). The remaining Re−O bond exhibited triple bond character (Re−O = 1.683(2) Å) with a simultaneous bond lengthening of the trans Re−N bond (Re−N(10′) = 2.238(2) Å).

Although a single-crystal X-ray structure could not be obtained for **16**, its structure could be elucidated by comparison of its NMR and IR data with that of **15**. The ^{1}H NMR spectrum of **15** revealed that, compared with that of the starting material [(4,7-diphenyl-1,10-phen)ReO_3Br] (**12**), the protons of the 4,7-diphenyl-1,10-phenanthroline ligand were nonequivalent and the protons on the phenathroline ring trans to the Re−O triple bond were assigned as upfield in the ^{1}H NMR spectrum. The ^{13}C NMR spectrum exhibited distinctive singlets for a [3 + 2] cycloaddition product (δ, 181.7 and 98.1 ppm) from the *C*O and *C*Ph_2 carbons of the cyclized ketene, respectively. The IR spectrum revealed a C═O stretch assigned to the carbonyl group at 1714 cm^{-1} and a characteristic Re−O stretch at 941 cm^{-1}. The ^{1}H NMR spectrum of **16** showed that the two dipyridyl rings were nonequivalent due to the loss of symmetry exhibited in starting material (**14**). The ^{13}C NMR spectrum of complex **16** exhibited the expected singlets for the *C*O and *C*Ph_2 carbons of the cyclized ketene (δ, 182.4 and 97.6 ppm), whereas the IR spectrum also showed the expected C═O stretch of a carbonyl group at 1710 cm^{-1} and one Re−O stretch at 974 cm^{-1}. Mass spectra and elemental analysis were also consistent with the existence of an addition product. In addition in the known [3 + 2] cycloaddition product **2**,[11] effectively the methyl analogue of **16**, the ^{13}C NMR shifts of the *C*O and *C*Ph_2 carbons are very similar (δ, 184.2 and 95.3 ppm). The carbonyl shift in complex **2** is at 1670 cm^{-1} compared to 1710 cm^{-1} in complex **16**, which we ascribe to the electron-withdrawing nature of the chloro ligand.

The single-crystal X-ray diffraction structure of **17** showed a trans arrangement of the two pyridine ligands (Figure 4). This infers that the correct structure for [(py)$_2$$ReO_3$Cl] (**14**), assuming there is no rapid pyridine ligand site exchange, could also have the pyridine ligands trans to each other (**A** in Figure 3). In **17**, the configuration is probably dictated by sterics between the pyridine ligands and bulky phenyl groups of the cyclized ketene. This structure is in contrast to the previously reported [3 + 2] cycloaddition product **3**,[11] in effect the methyl analogue of **17**. Unfortunately, no single-crystal X-ray diffraction structure was obtained for complex **3** and the pyridine ligands were assigned cis, but we believe there is a distinct possibility that the two pyridine ligands also lie trans to each other in complex **3**.

Summary

Despite the possibility of the mode of cycloaddition between rhenium trioxo complexes and ketene being dictated by the ligand set around the metal, the reaction of diphenyl ketene with six rhenium trioxo complexes led to the isolation of a single series of novel [3 + 2] cycloaddition products. The diverse ligand sets of scorpionates hydridotris(pyrazolyl)borate, phenyltris(pyrazolyl)borate, and tris(1-pyrazolyl)methane and pyridines 4,7-diphenyl-1,10-phenanthroline, 4,4′-di-*tert*-butyl-2,2′-dipyridine, and pyridine led to identical cyclization modes. This was confirmed in five of the six products by single-crystal X-ray diffraction and in all cases by ^{13}C NMR and IR spectroscopies. In all cases, the products were regioselective, showing reaction across the ketene C═C double bond in preference to reaction with the ketene C═O double bond. The control of alternative cyclization modes is being explored between ketene and other metal oxo complexes, the results of which will be reported in due course.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra (PDF) for all compounds and CIF for compounds **9**−**11**, **15**, and **17**. This material is available free of charge via the Internet at http://pubs.acs.org.

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