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Reactivity studies on bimetallic μ-malonyl complexes: cleavage and alkylation chemistry of the malonyl ligand

Joseph M. O'Connor, Roger Uhrhammer, Raj K. Chadha and Barbara Tsuie

Department of Chemistry, 0506 University of California San Diego La Jolla, CA 92093 (USA)

Arnold L. Rheingold

Department of Chemistry University of Delaware Newark, DE 19716 (USA)

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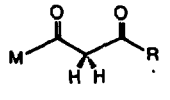
Abstract

The bimetallic μ-malonyl complexes: $\{(\eta^5\text{-}C_5Me_5)(NO)(PPh_3)Re[\mu\text{-}(COCH_2CO)\text{-}C^1:C^3]Re(CO)_4(Br)\}^-Li^+$ (**1**), $\{(\eta^5\text{-}C_5Me_5)(NO)(PPh_3)Re[\mu\text{-}(COCH_2CO)\text{-}C^1:C^3]Re(CO)_4(PMe_3)\}\cdot Li^+OSO_2CF_3^-$ (**2**), and $(\eta^5\text{-}C_5Me_5)(NO)(PPh_3)Re[\mu\text{-}COCH_2CO)\text{-}C^1,O^3:C^3]Re(CO)_4$ (**3**) undergo carbon–carbon bond cleavage reactions of the malonyl ligand upon exposure to HCl. Deprotonation of $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(\mu\text{-}\eta^1,\eta^2\text{-}COCH_2CO)Re(CO)_4$ (**3**), in THF solution and addition of CH_3I leads to the C-alkylation product, $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)[\mu\text{-}(COCH(CH_3)CO)\text{-}C^1,O^3:C^3]Re(CO)_4$ (**11**), isolated as a single diastereomer (85% yield). Deprotonation of **11** and alkylation with CD_3I leads to $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)[\mu\text{-}(COC(CH_3)(CD_3)CO)\text{-}C^1,O^3:C^3]Re(CO)_4$ (**12-d_3**) with > 97% diastereoselectivity. Alkylation of the enolate anion derived from deprotonation of **11** with ethyl iodide led to isolation of $(\eta^5\text{-}C_5Me_5)(NO)(PPh_3)Re\{\mu\text{-}[COCCH_3{=}C(OCH_2CH_3)]\text{-}C^1,O^3:C^3\}Re(CO)_4$ (**21**) in 84% yield. Quenching of the enolate anion of **3** with excess ethyl iodide led to formation of an 11:89 mixture of $(\eta^5\text{-}C_5Me_5)(NO)(PPh_3)Re[\mu\text{-}(COCHCH_2CH_3CO)\text{-}C^1:C^3,O^3]Re(CO)_4$ (**15**) and $(\eta^5\text{-}C_5Me_5)(NO)(PPh_3)Re[\mu\text{-}(COCH{=}COCH_2CH_3)\text{-}C^1,O^3:C^3]Re(CO)_4$ (**16**) in 87% combined yield. When the enolate anion of **3** was treated with allyl bromide, both *C* and *O* alkylation products $(\eta^5\text{-}C_5Me_5)(NO)(PPh_3)Re\{\mu\text{-}[COCH(CH_2CH{=}CH_2)CO]\text{-}C^1:C^3,O^1\}Re(CO)_4$ (**17**) and $(\eta^5\text{-}C_5Me_5)(NO)(PPh_3)Re\{\mu\text{-}[COCH{=}C(OCH_2CH{=}CH_2)]\text{-}C^1,O^3:C^3\}Re(CO)_4$ (**18**) were formed in a 32:68 ratio (84% combined yield). Alkylation with benzyl bromide gave $(\eta^5\text{-}C_5Me_5)(NO)(PPh_3)Re[\mu\text{-}(COCH{=}COCH_2C_6H_5)\text{-}C^1,O^3:C^3]Re(CO)_4$ (**19**) in 76% yield.

1. Introduction

β-Oxoacyl and μ-malonyl (**I** and **II**) complexes are of interest both as reactive intermediates in organic synthesis and as models for carbon monoxide homologation chemistry. We recently reported the preparation of the first bimetallic μ-malonyl complexes: $\{(\eta^5\text{-}C_5Me_5)(NO)(PPh_3)Re[\mu\text{-}(COCH_2CO)\text{-}C^1:C^3]Re(CO)_4(Br)\}^-Li^+$ (**1**), $\{(\eta^5\text{-}C_5Me_5)(NO)(PPh_3)Re[\mu\text{-}(COCH_2CO)\text{-}C^1:C^3]Re(CO)_4(PMe_3)\}\cdot Li^+OSO_2CF_3^-$ (**2**), and $(\eta^5\text{-}C_5Me_5)(NO)(PPh_3)Re[\mu\text{-}(COCH_2CO)\text{-}C^1,O^3:C^3]Re(CO)_4$ (**3**), from reaction of the rhenium enolate $(\eta^5\text{-}C_5Me_5)(PPh_3)(NO)Re(COCH_2Li)$ (**4**) [1] and metal carbonyl electrophiles (Scheme 1) [2]. Here we report details on the reactivity of the μ-malonyl ligand in **1**, **2**, and **3**, including the acid-induced fragmentation of the malonyl ligand and the alkylation chemistry of μ-malonate anions. Portions of this work have appeared in preliminary form [2d].



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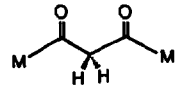

II

2. Results

2.1. Reactivity of μ-malonyl compexes with electrophilic reagents

The μ-malonyl complexes **1**, **2**, and **3** underwent reaction with HCl to give mononuclear products resulting from cleavage of a carbon–carbon bond in the malonyl ligand. ^1H NMR spectroscopy of the crude reaction mixture which resulted from addition of excess anhydrous HCl (0.9 M) to a yellow CH_2Cl_2 slurry

Correspondence to: Dr. J.M. O'Connor or Professor A.L. Rheingold.

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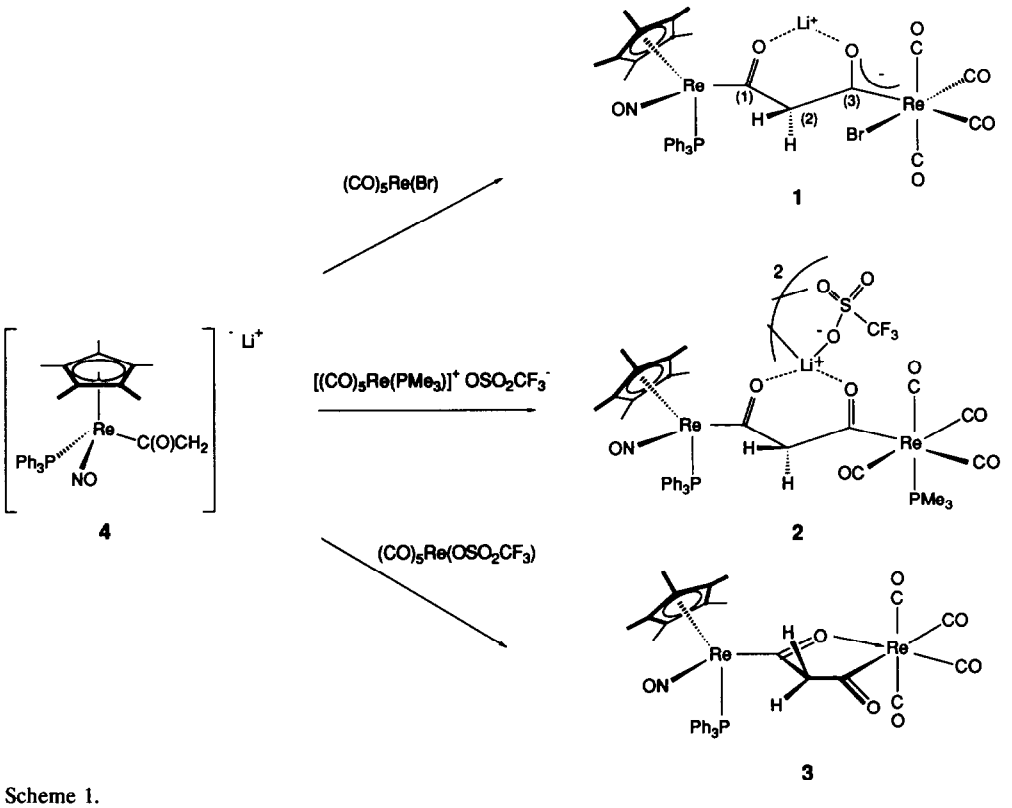
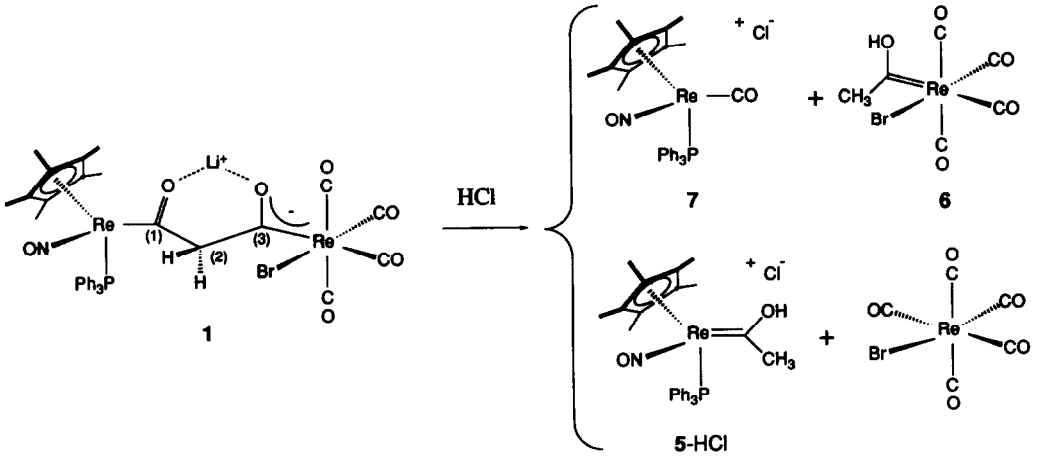
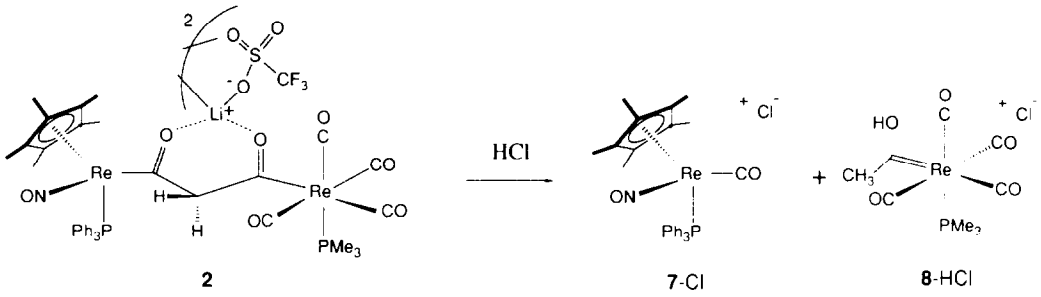


Scheme 1.

of **1** (26 mg, 34 mM) indicated the presence of three compounds: $[(\eta^5\text{-}C_5Me_5)(NO)PPh_3)Re{=}C(OH)\text{-}CH_3]^+Cl^-$ (**5** · HCl) [3], mononuclear carbonyl cis-$(CO)_4BrRe{=}C(OH)CH_3$ (**6**) [4], and $[(\eta^5\text{-}C_5Me_5)\text{-}(NO)(PPh_3)Re(CO)]^+Cl^-$ (**7**) [5] in a 34:66:66 ratio. The ^1H NMR resonances for these products were identical to authentic samples, prepared as described below. The formation of $(CO)_5ReBr$ was also indicated by IR spectroscopy on the crude reaction mixture. When one equivalent of HCl was added to a THF solution of **1** (25.4 mg, 48 mM), the cleavage products $(\eta^5\text{-}C_5Me_5)(NO)(PPh_3)Re(COCH_3)$ (**5**) [3] and **7** were observed in a 33:67 ratio by ^1H NMR spectroscopy ($CDCl_3$). Thus, **5** · HCl observed in the previous reac-



Scheme 2.

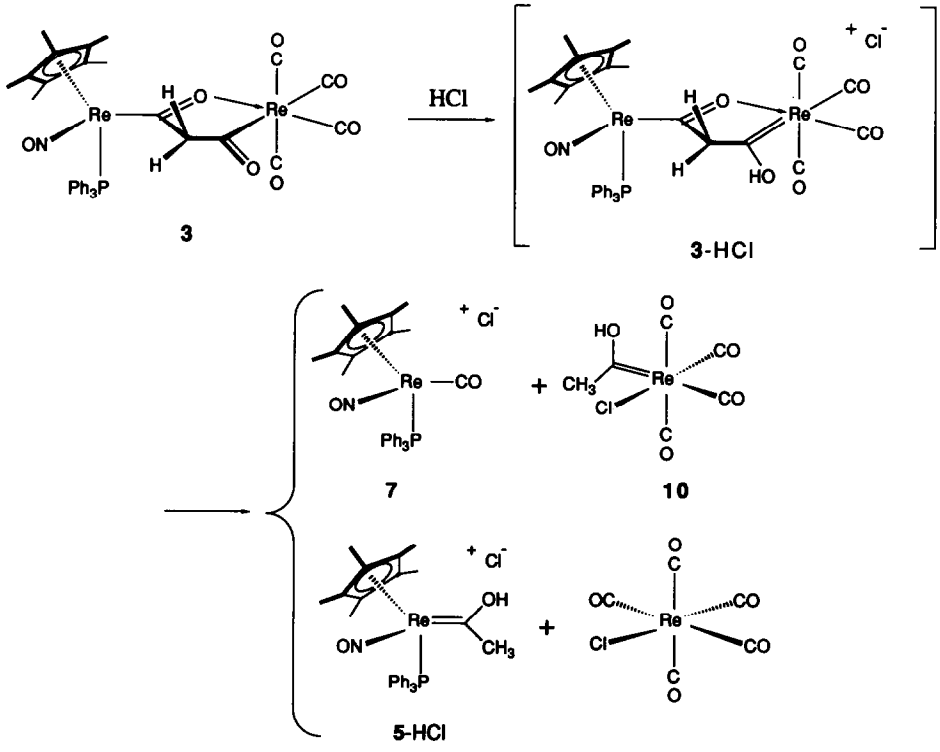


Scheme 3.

tion was the result of protonation of acyl **5** by excess acid. Low temperature ^{1}H NMR spectroscopy of a sample resulting from addition of 1 equiv. of CF_3CO_2H to a 63 mM THF-d_8 solution of **1** · TMEDA at −78°C indicated only malonyl cleavage products with no evidence of a protonated form of **1** (Scheme 2).

Hydroxycarbene complex **5** · HCl was independently prepared by reaction of the known acyl complex **5** and HCl. A low field carbene resonance at 296.6 ppm was observed in the ^{13}C NMR spectrum ($CDCl_3$) of **5** · HCl, and the hydroxyl hydrogen resonance was observed as a broad singlet at δ 15.59 in the ^{1}H spectrum ($CDCl_3$). The known hydroxycarbene complex, *cis*-$(CO)_4BrRe{=}C(OH)CH_3$ (**6**) [4], was independently prepared by sequential reaction of $(CO)_5ReBr$ with MeLi, and HCl. As observed for **5** · HCl, a downfield hydroxyl hydrogen resonance was observed (δ 15.14) in the ^{1}H NMR spectrum ($CDCl_3$) of **6**, and the carbene carbon resonance was observed at 319.3 ppm in the $^{13}C\{^1H\}$ NMR spectrum.

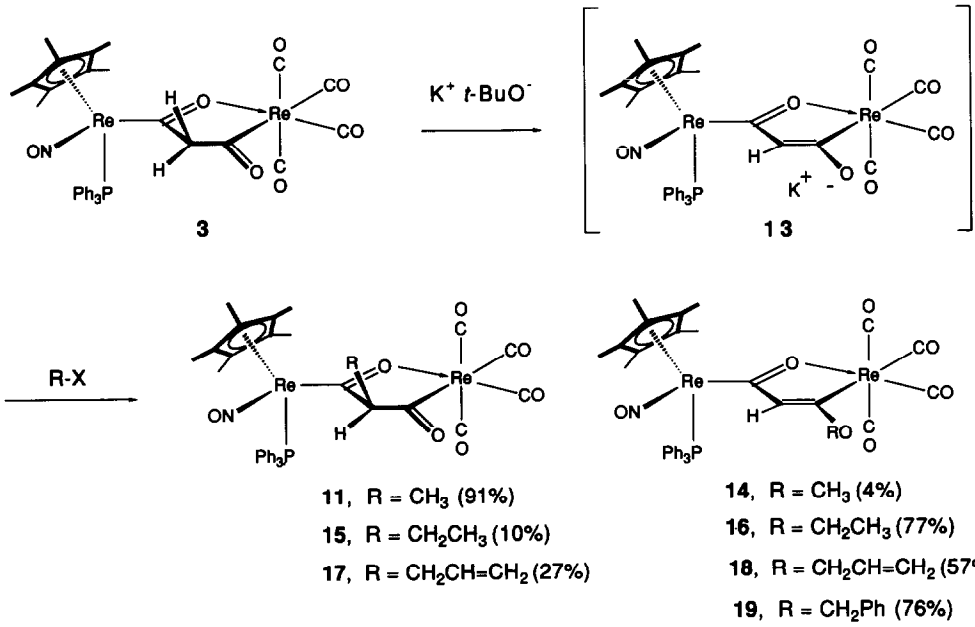
Reaction of the neutral μ-malonyl $\{(\eta^5\text{-}C_5Me_5)(NO)(PPh_3)Re[\mu\text{-}(COCH_2CO)\text{-}C^1:C^3]Re(CO)_4(PMe_3)\} \cdot Li^+OTf^-$ (**2**, $OTf^- = O_3SCF_3^-$) (14.9 mg, 15 mM) with HCl in CH_2Cl_2 solution led to only two mononuclear cleavage products (Scheme 3). The sole products observed by ^{1}H NMR spectroscopy of the crude reaction mixture were **7** and the new hydroxycarbene complex $[cis\text{-}(CO)_4(PMe_3)Re{=}C(OH)CH_3]^+Cl^-$



Scheme 4.

(**8**-HCl). In a separate experiment, addition of 1 equiv. of HCl to a 9 mM THF solution of **2** resulted in the formation of *cis*-$(CO)_4(PMe_3)Re(COCH_3)$ (**8**) and **7** as the sole products, as determined by ^1H NMR spectroscopy. An authentic sample of **8**-HCl was prepared by reaction of **8** with HCl. The hydroxyl hydrogen resonance of **8** · HCl appeared as a broad singlet at δ 15.46 in the ^1H NMR spectrum ($CDCl_3$), and the carbene carbon resonance was observed at 294.2 ppm in the $^{13}C\{^1H\}$ NMR spectrum. Complex **8** was itself prepared from addition of CH_3MgBr to $[(CO)_5Re\text{-}PMe_3]^+OTf^-$. The *cis* geometry in **8** is consistent with the presence of three terminal carbonyl carbon resonances in a 1:1:2 ratio of intensities, and an acyl carbon resonance coupled to a *cis* phosphorus at 257.5 (d, $J = 10.9$) ppm in the $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$) of **8**. The downfield shift of the carbene carbon of **8** · HCl at 294.2 ppm from 257.5 in **8** is consistent with conversion of an acyl to a carbene moiety. Complex **8** · HCl undergoes loss of HCl to regenerate **8** when placed under high vacuum overnight.

In contrast to **1** and **2**, chelating μ-malonyl **3** is relatively stable in the presence of excess HCl at room temperature (Scheme 4). Addition of ~7 equiv. of anhydrous HCl to a $CDCl_3$ solution of **3** (50 mM) resulted in protonation on the η^1-acyl oxygen of **3**, to generate $\{(\eta^5\text{-}C_5Me_5)(NO)(PPh_3)Re[\mu\text{-}COCH_2\text{-}C(OH)\text{-}C^1,O^3,C^3]Re(CO)_4\}^+Cl^-$ (**3** · HCl). In the ^1H NMR spectrum of this solution, the methylene hydrogen resonances were broadened and shifted to lower field from those of **3**. In addition, the two methylene hydrogen resonances were broadened by different amounts due to different rates of exchange *via* enolization [2]. The more labile *exo* hydrogen (distal to the PPh_3 ligand), is observed as the broader of the two resonance (δ 3.57, $\nu_{1/2} = 84$ Hz), while the *endo*-methylene hydrogen resonance remains as a relatively sharp signal (δ 2.96, $\nu_{1/2} = 10$ Hz). The acid catalyzed exchange of the methylene hydrogens is retarded at lower temperatures and the characteristic AB pattern is reestablished. After removal of the volatiles and exposure to high vacuum overnight, malonyl **3** is recovered in over 76% yield. Addition of > 30 equiv. of HCl to a $CDCl_3$ solution of **3** (0.13 M) greatly catalyzed proton exchange to the extent that the methylene hydrogen resonances were broadened into the baseline at room temperature. The low temperature $^{13}C\{^1H\}$ NMR (−40°C) spectrum of this mixture indicated that **3** was quantitatively protonated at the η^1-acyl oxygen, and only one set of resonances, corresponding to **3** · HCl, was observed. The C^3-acyl carbon resonance of **3** undergoes a shift to low field from 275.6 ppm to 321.7 in **3** · HCl, characteristic of a carbene carbon. The C^1-acyl carbon and the four terminal carbonyl carbon resonances of **3** were only slightly shifted upon protonation. In the IR spectrum (CH_2Cl_2) of a sample of **3** which had been exposed to HCl gas, multiple bands were observed between 2100 and 1923, the $\nu(C^3{=}O^3)$ band at 1615 is greatly diminished in intensity, and the bands at 1481w, 1391m, 1372m, and 1343w cm^{-1} are virtually unchanged from those of **3**. Attempts to crystallize **3** · HCl were unsuccessful and only pure **3** was recov-



Scheme 5.

ered. However, when allowed to stand overnight at room temperature in the presence of HCl, decomposition occurred to give a 91:9 mixture of **5** · HCl and **7** in 79% yield. Also observed were minor amounts (4%) of a compound tentatively identified as the hydroxycarbene complex *cis*-$(CO)_4(Cl)Re{=}C(OH)CH_3$ (**10**), on the basis of a methyl singlet at δ 3.19 in the ^1H NMR spectrum ($CDCl_3$).

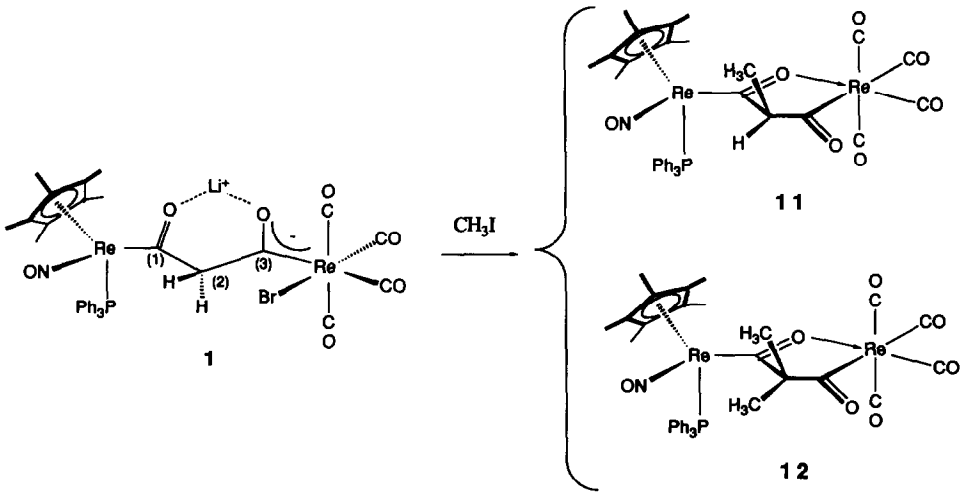
Treatment of malonyl complex **1** (10 mg, 19 mM) with methyl iodide (0.2 M) in THF-d_8 solution failed to give identifiable malonyl ligand cleavage products. After 1 day, ^1H NMR spectroscopy on the sample indicated the presence of unreacted **1** (43%), methylated malonyl complexes $(\eta^5\text{-}C_5Me_5)(NO)(PPh_3)Re[\mu\text{-}(COCHCH_3CO)\text{-}C^1:C^3,O^1]Re(CO)_4$ (**11**, < 10%) and $(\eta^5\text{-}C_5Me_5)(NO)(PPh_3)Re[\mu\text{-}(COC(CH_3)_2CO)\text{-}C^1:C^3,O^1]Re(CO)_4$ (**12**, ~ 23%), as well as a number of resonances due to unidentified products (Scheme 5). Neutral malonyl complex **2** (24.4 mg, 33 mM) also underwent slow reaction with 1.9 equiv. of CH_3I (64 mM) in $CDCl_3$ solution. After 4 days, ^1H NMR spectroscopy on the mixture revealed the presence of unreacted **2** (60%) as well as a 20% yield of **7**.

2.2. Deprotonation / alkylation chemistry

Having previously characterized the enolization chemistry of **3** and noting the stereoselective incorporation of deuterium into the methylene sites of the malonyl ligand [2], we examined the formation of new carbon–carbon bonds through the deprotonation/alkylation chemistry of μ-malonyl complexes [2d]. Deprotonation of **3** (9 mM) in THF solution with ^{t}BuOK (13 mM) generates the enolate anion $(\eta^5\text{-}C_5Me_5)(NO)(PPh_3)Re[\mu\text{-}(COCH{=}CO)\text{-}C^1,O^3:C^3]Re(CO)_4\}^-K^+$ (**13**), as previously described [2f]. Quenching of **13** with excess methyl iodide led to a rapid change in the solution color from deep orange to yellow and the precipitation of KI. Examination of the crude reaction mixture by ^1H NMR spectroscopy indicated the formation of $(\eta^5\text{-}C_5Me_5)(NO)(PPh_3)Re[\mu\text{-}(COCHCH_3CO)\text{-}C^1:C^3,O^1]Re(CO)_4$ (**11**) as a single diastereomer in 91% isolated yield (Scheme 6). In addition to **11**, the *O*-alkylation product $(\eta^5\text{-}C_5Me_5)(NO)(PPh_3)Re[\mu\text{-}(COCH{=}COCH_3)\text{-}C^1,O^3:C^3]Re(CO)_4$ (**14**) was formed in ~ 4% yield. The spectroscopic features of **3** and **11** are nearly identical, except for the obvious differences expected for a methyl substitution on the methylene carbon of the malonyl ligand. An observed coupling constant of 7 Hz between the methine and the methyl group clearly establishes **11** as a *C*-alkylated product. In the ^{13}C NMR spectrum (CD_2Cl_2) of **11** the malonyl carbons bound to rhenium are observed at 298.7 (d, $J = 7$) and 276.5 ppm, while the C^1 and C^3 counterparts in **3** are observed at 290 (d) and 276 ppm. The presence of phosphorus coupling to C^1 allows for easy assignment of the C^1 and C^3 resonances. In the IR spectrum of **11**, bands were observed at 2080, 1969, 1922, 1660, and 1608 cm^{-1}, compared to the corresponding bands at 2080, 1972, 1923, 1664, and 1615 cm^{-1} for **3**.

Complex **14** was independently prepared in 42% isolated yield from reaction of **13** with the more reactive alkylation reagent, methyl triflate. In the ^{13}C NMR spectum ($CDCl_3$) of **14**, acyl carbon C^3 appeared as a resonance at 271.4 (d, $J = 9$) ppm and the enol ether carbon C^1 was located at 224.4 ppm.

Quenching of enolate **13** with excess ethyl iodide led to formation of an 11:89 mixture of $(\eta^5\text{-}C_5Me_5)(NO)(PPh_3)Re[\mu\text{-}(COCHCH_2CH_3CO)\text{-}C^1:C^3,O^3]$-



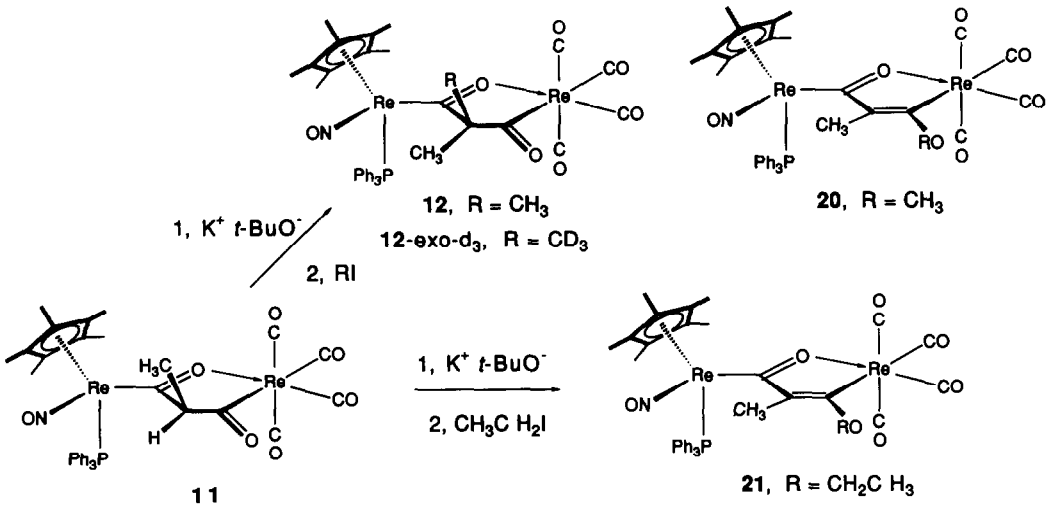
Scheme 6.

$Re(CO)_4$ (**15**) and $(\eta^5\text{-}C_5Me_5)(NO)(PPh_3)Re[\mu\text{-}(COCH{=}COCH_2CH_3)\text{-}C^1,O^3 : C^3]Re(CO)_4$ (**16**) in 87% combined yield, as determined by ^1H NMR spectroscopy on the crude reaction mixture, after filtering through celite. The *C*- and *O*-alkylation products were easily separated on the basis of their differing solubilities and subsequently characterized. Their spectroscopic properties were similar to those of previously described μ-malonyl and enol-ether derivatives. One distinguishing spectroscopic difference between **15** and **16** was the ^1H NMR resonances for the diastereotopic methylene hydrogens of the newly introduced ethyl group; in **15** they appeared as eight line multiplets at δ 3.89 and 3.74, while in **16** they appeared together as a multiplet at δ 1.60. As was observed for **11**, complex **16** was isolated as only one diastereomer as determined by ^1H NMR spectroscopy.

When **13** was treated with excess allyl bromide, both *C*- and *O*-alkylation products $(\eta^5\text{-}C_5Me_5)(NO)(PPh_3)Re\{\mu\text{-}[COCH(CH_2CH{=}CH_2)CO]\text{-}C^1 : C^3,O^1\}Re(CO)_4$ (**17**) and $(\eta^5\text{-}C_5Me_5)(NO)(PPh_3)Re\{\mu\text{-}[COCH{=}C(OCH_2CH{=}CH_2)]\text{-}C^1,O^3 : C^3\}Re(CO)_4$ (**18**) were formed in a 32:68 ratio (84% combined yield), as determined by ^1H NMR spectroscopy. Complex **18** was characterized by ^1H, ^{13}C NMR, IR, and mass spectroscopies, as well as by microanalysis. Complex **17** was not isolated, but its presence was suggested by a unique set of C_5Me_5 and allyl resonances with diastereotopic methylene hydrogens in the ^1H NMR spectrum of the crude reaction mixture. When **13** was treated with excess benzyl bromide, $(\eta^5\text{-}C_5Me_5)(NO)(PPh_3)Re[\mu\text{-}(COCH{=}COCH_2C_6H_5)\text{-}C^1,O^3 : C^3]Re(CO)_4$ (**19**) was isolated as the sole product (76% yield).

Introduction of a second methyl group at carbon proceeds with excellent regioselectivity. When complex **11** was first deprotonated with ^{t}BuOK and then treated with methyl iodide, dimethyl μ-malonyl $(\eta^5\text{-}C_5Me_5)(NO)(PPh_3)Re[\mu\text{-}(COC(CH_3)_2CO)\text{-}C^1 : C^3,O^1]Re(CO)_4$ (**12**) was isolated in 85% yield (Scheme 7). Also observed in this reaction was the *O*-alkylation product $(\eta^5\text{-}C_5Me_5)(NO)(PPh_3)Re\{\mu\text{-}[COCCH_3{=}C(OCH_3)]\text{-}C^1,O^3 : C^3\}Re(CO)_4$ (**20**) in ~4% yield, by ^1H NMR spectroscopy on the crude reaction product. That **12** is a μ-malonyl complex is supported by two low field carbonyl resonances in the ^{13}C NMR spectrum at 304.8 (d, $J = 8$) and 277.8 ppm. In addition, the IR spectrum (CH_2Cl_2) displayed an η^1-acyl stretch at 1600 cm^{-1}. The *O*-alkylation product **20** (40% yield) was prepared independently by deprotonation of **11** with ^{t}BuOK followed by addition of $Me_3O^+BF_4^-$.

In the ^1H NMR spectrum ($CDCl_3$) of **12**, the diastereotopic methyl groups were observed as singlets at δ 0.03 (3H) and 0.95 (3H). The high field signal corresponds to the methyl group on the *endo*-face (proximal to the PPh_3 ligand) of the malonyl chelate ring, which places this group into the shielding region of the adjacent phenyl rings. The low field signal (δ 0.95) then corresponds to the *exo*-face methyl group. The stereochemical assignment by chemical shift arguments were supported by the results of NOE experiments in chloroform-*d* solution. Saturation of the C_5Me_5 resonance at δ 1.68 resulted in a 3.2% increase in intensity of the 0.95 singlet and a 1.4% increase in the 0.03 singlet. Saturation of the PPh_3 signals resulted in a 0.8% increase in the δ 0.95 singlet and 3.5% increase in the 0.03 singlet. Likewise, saturation of the δ 0.03 singlet



Scheme 7.

TABLE 1. Crystal and data collection, refinement parameters for **11** and **12**

	11	**12**
Formula	$C_{36}H_{34}NO_7PRe_2$	$C_{37}H_{36}NO_7PRe_2$
Lattice type	Triclinic	Monoclinic
Space group	*P*1	*C*2/*c*
a (Å)	10.295 (3)	17.220 (5)
b (Å)	11.096 (3)	12.984 (2)
c (Å)	17.367 (6)	32.584 (3)
α (°)	73.30 (2)	-
β (°)	87.39 (2)	94.45 (2)
γ (°)	70.62 (2)	-
V (Å^3)	1790.1 (9)	7263 (2)
Z	2	8
Crystal dimensions (mm^3)	0.26 × 0.26 × 0.26	0.10 × 0.14 × 0.31
Crystal color	Yellow	Yellow
D_{calc} (g cm^{-3})	1.848	1.847
μ	72.33 (Mo Kα) cm^{-1}	13.170 (Cu Kα) mm^{-1}
Temperature (°C)	23	23
$T_{(max)}/T_{(min)}$	2.08	0.1714/0.3361
Radiation type	Mo Kα (λ = 0.71073 Å)	Cu Kα (λ = 1.54184 Å)
2θ range (°)	40–50	4–110
Read	6617	4997
Unique	6289	4585
Unique observed	4468	3993
R (F) (%)	4.95	4.42
R (*wF*) (%)	5.19	6.33
GOF	1.153	1.91
Δ (ρ) (e Å^{-3})	2.3	2.8

resulted in a 0.5% increase in the C_5Me_5 resonance and a 2.4% increase in the PPh_3 resonance. Finally, saturation of the δ 0.95 singlet resulted in a 2.8% increase in the C_5Me_5 resonance and a 2.1% increase in the PPh_3 resonance. While these observed NOEs are small, they are consistent with the stereochemical assignment.

To probe the kinetic stereoselectivity of alkylation, the potassium enolate of **11** was quenched with CD_3I to give a > 38:1 mixture of non-enolizable diastereomers **12**-*exo*-d_3 and **12**-*endo*-d_3 (Scheme 7). The major product, **12**-*exo*-d_3, has the deuterio-methyl group on the *exo*-face of the malonyl ligand. In the ^{1}H NMR spectrum ($CDCl_3$) of this mixture, a methyl singlet is observed at δ 0.03 (corresponding to **12**-*exo*-d_3), while its geminal partner at δ 0.95 (corresponding to **12**-*endo*-d_3) is nearly absent. In the ^{2}H{^{1}H} NMR spectrum ($CHCl_3$) a singlet at δ 1.00 was assigned to the *endo* methyl group. In a similar fashion, methylation (CH_3I) of the enolate anion derived from deprotonation of **11**-d_3 resulted in a > 38:1 ratio of diastereomers **12**-*endo*-d_3 and **12**-*exo*-d_3.

Alkylation of the enolate anion derived from deprotonation of **11** with ethyl iodide led to isolation of $(\eta^5$-$C_5Me_5)$(NO)(PPh_3)Re{μ-[COCCH$_3$=(OCH$_2$-CH$_3$)]-C^1,O^3:C^3}Re(CO)$_4$ (**21**) in 84% yield after silica gel chromatography.

2.3. X-Ray structure of $(\eta^5$-$C_5Me_5)(NO)(PPh_3)Re[\mu$-$(COCHCH_3CO)$-$C^1$:$C^3$,$O^1]Re(CO_4)$ (11)

The relative stereochemistry of **11** could not be unambiguously assigned from the spectroscopic data, and we therefore turned to single crystal X-ray analysis [8]. X-Ray data were acquired on a yellow crystal of **11**, obtained by cooling a concentrated CH_2Cl_2 solution layered with hexanes. Crystal data, data collection, and refinement parameters are given in Table 1. Selected bond distances and angles are given in Table 2. From the structure shown in Fig. 1, the relative stereochemistry of **11** is *SR*,*RS* [6 *]. The ON–Re–C_α–O torsion angle (θ) is 179°, which places the C(11)–O(2) acyl oxygen anti to the NO ligand. The methyl substituent C(13) sits on the less congested *exo*-face of the nearly planar μ-malonyl chelate ring, directed distal to the PPh_3 ligand. There is only a slight degree of puckering

* Reference number with asterisk indicates a note in the list of references.

TABLE 2. Selected bond distances (Å) and angles (°) for **11**

(a) Bond distances			
Re(2)–C(15)	1.978(14)	O(2)–C(11)	1.175(13)
Re(2)–C(16)	1.978(8)	C(11)–C(12)	1.586(20)
Re(2)–C(17)	1.950(17)	C(12)–C(14)	1.584(15)
Re(2)–C(18)	2.003(14)	N–O(1)	1.187(14)
Re(2)–C(14)	2.153(13)	C(15)–O(15)	1.145(17)
Re(2)–O(2)	2.180(6)	C(16)–O(16)	1.126(24)
C(12)–C(13)	1.547(19)	C(17)–O(17)	1.105(18)
Re(1)–P	2.378(3)	C(18)–O(18)	1.101(18)
Re(1)–N	1.778(11)	C(14)–O(3)	1.213(19)
Re(1)–C(11)	2.035(9)		
(b) Bond angles			
C(15)–Re(2)–C(16)	89.4(7)	C(13)–C(12)–C(14)	106.6(9)
C(15)–Re(2)–C(17)	85.2(6)	C(11)–C(12)–C(13)	110.3(12)
C(15)–Re(2)–C(18)	173.4(6)	Re(1)–N–O(1)	171.0(11)
C(15)–Re(2)–C(14)	89.3(5)	N–Re(1)–P	90.8(4)
C(15)–Re(2)–O(2)	95.2(4)	N–Re(1)–C(11)	98.7(5)
C(16)–Re(2)–C(17)	93.7(7)	P–Re(1)–C(11)	88.1(3)
C(16)–Re(2)–C(18)	93.9(7)	Re(1)–C(11)–O(2)	127.5(10)
C(14)–Re(2)–C(16)	168.3(5)	Re(1)–C(11)–C(12)	118.9(7)
C(16)–Re(2)–O(2)	92.4(5)	C(12)–C(11)–O(2)	113.5(9)
C(17)–Re(2)–C(18)	88.9(6)	C(14)–C(12)–C(11)	111.4(10)
C(14)–Re(2)–C(17)	97.8(6)	Re(2)–O(2)–C(11)	125.9(9)
C(17)–Re(2)–O(2)	173.9(6)	Re(2)–C(14)–O(3)	132.9(8)
C(14)–Re(2)–C(18)	88.5(5)	Re(2)–C(14)–C(12)	111.2(9)
C(18)–Re(2)–O(2)	90.3(4)	O(3)–C(14)–C(12)	116.0(11)
C(14)–Re(2)–O(2)	76.1(4)		

of the five-membered chelate ring containing Re(2)–O(2)–C(11)–C(12)–C(14). Dihedral angles of −69° and 73° for Re(1)–C(11)–C(12)–C(13) and C(13)–C(12)–C(14)–O(3) indicate that C(12) is puckered upwards away from the triphenylphosphine ligand.

2.4. X-Ray structure of $(\eta^5\text{-}C_5Me_5)(NO)(PPh_3)Re[\mu\text{-}(COC(CH_3)_2CO)\text{-}C^1:C^3,O^1]Re(CO)_4$ (12)

To determine if a quaternary carbon center β to the metal would cause a distortion away from an anti conformation, an X-ray crystal structure determination was carried out on **12** [9]. X-Ray data were acquired on a yellow crystal of **12** obtained from diffusion of pentane into a CH_2Cl_2 solution at 5°C to give the structure shown in Fig. 2. Crystal data, data collection, and refinement parameters are given in Table 1. Selected bond distances and angles are presented in Table 3. The θ value observed for **12** is 178.1°. Any steric interaction between the *endo*-methyl group C(13) and the PPh_3 ligand is compensated by a slight opening of the C(11)–Re(1)–P(1) bond angle to 91.1° (3). The corresponding angle in **2** is 87.2° (1). From the mean plane of the malonyl chelate ring [Re(2)–O(2)–C(11)–C(12)–C(15)], C(12) is puckered away from the PPh_3 ligand by nearly one-tenth of an Å. Tipping of C(12) away from the PPh_3 ligand is also indicated by the dihedral angles for P(1)–Re(1)–C(11)–C(12) of

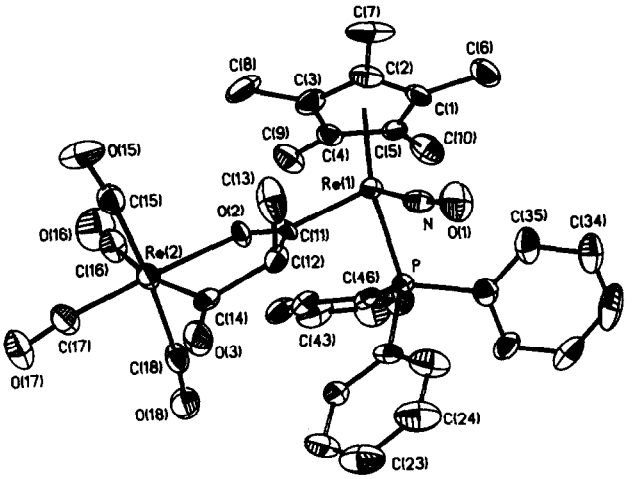


Fig. 1. Structure of $(\eta^5\text{-}C_5Me_5)(NO)(PPh_3)Re[\mu\text{-}(COCHCH_3CO)\text{-}C^1:C^3, O^1]Re(CO)_4$ (**11**).

−108.3° and for P(1)–Re(1)–C(11)–O(2), 85.6°. The bonding of the malonyl ligand to the metals is comparable to that observed for complex **3**; the Re(1)–C(11) distance of 2.051 (10) Å is shorter than the Re(2)–C(15) bond length of 2.118 (11) Å, and the Re(2)–O(2) distance is 1.279 (11) Å.

3. Discussion

The cleavage of the carbon–carbon bond in mononuclear β-oxoacyl complexes was previously proposed by Davies in mononuclear iron systems (Schemes 8 and 9) [10]. Acidic hydrolysis of **22** led to iron carbonyl $[(\eta^5\text{-}C_5H_5)(CO)_2(PPh_3)Fe]^+$ (**24**) and acetaldehyde. Presumably acyl-aldehyde **23** (R = H) was

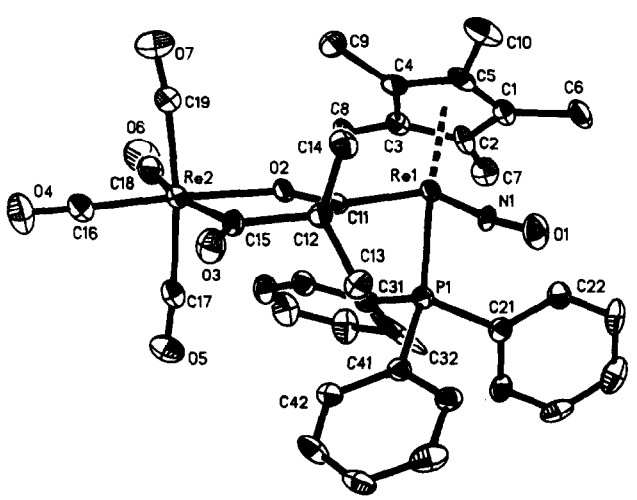


Fig. 2. X-Ray structure of $(\eta^5\text{-}C_5Me_5)(NO)(PPh_3)Re[\mu\text{-}(COC(CH_3)_2CO)\text{-}C^1:C^3, O^1]Re(CO)_4$ (**12**).

TABLE 3. Selected bond distances (Å) and angles (°) for **12**

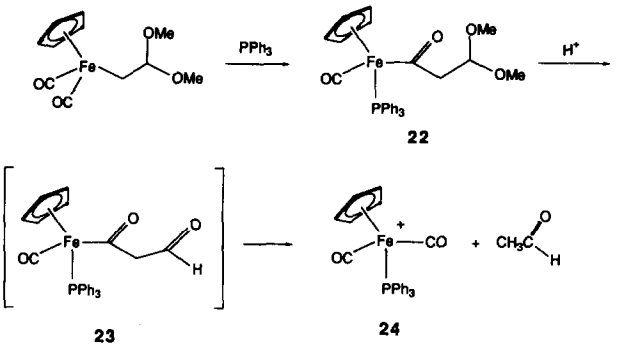
(a) Bond lengths			
Re(2)–C(19)	1.973(13)	O(2)–C(11)	1.279(11)
Re(2)–C(18)	1.988(14)	C(11)–C(12)	1.586(20)
Re(2)–C(16)	1.923(14)	C(12)–C(14)	1.539(14)
Re(2)–C(17)	1.978(13)	N(1)–O(1)	1.208(11)
Re(2)–C(15)	2.118(11)	Re(1)–C(11)	2.051(10)
Re(2)–O(2)	2.157(6)	C(12)–C(13)	1.527(15)
C(12)–C(14)	1.557(14)	C(16)–O(4)	1.156(19)
Re(1)–P(1)	2.392(3)	C(17)–O(5)	1.144(16)
Re(1)–N(1)	1.737(8)	Re(1)–CNT [a]	1.993
(b) Bond angles			
C(18)–Re(2)–C(19)	92.7(6)	C(14)–C(12)–C(15)	105.5(8)
C(16)–Re(2)–C(19)	84.4(6)	C(11)–C(12)–C(14)	108.8(8)
C(17)–Re(2)–C(19)	170.6(5)	Re(1)–N(1)–O(1)	170.4(8)
C(15)–Re(2)–C(19)	87.5(5)	N(1)–Re(1)–P(1)	92.2(3)
C(19)–Re(2)–O(2)	96.8(4)	N(1)–Re(1)–C(11)	99.1(4)
C(16)–Re(2)–C(18)	96.9(6)	P(1)–Re(1)–C(11)	91.1(3)
C(17)–Re(2)–C(18)	91.8(5)	Re(1)–C(11)–O(2)	117.5(7)
C(15)–Re(2)–C(18)	166.6(5)	Re(1)–C(11)–C(12)	126.9(6)
C(18)–Re(2)–O(2)	90.0(5)	C(12)–C(11)–O(2)	114.4(8)
C(16)–Re(2)–C(17)	86.9(6)	C(15)–C(12)–C(11)	110.0(8)
C(15)–Re(2)–C(16)	96.5(5)	Re(2)–O(2)–C(11)	123.3(6)
C(16)–Re(2)–O(2)	173.0(5)	Re(2)–C(15)–O(3)	130.4(8)
C(15)–Re(2)–C(17)	90.1(4)	Re(2)–C(15)–C(12)	114.2(7)
C(17)–Re(2)–O(2)	91.5(4)	O(3)–C(15)–C(12)	115.4(9)
C(15)–Re(2)–O(2)	76.7(3)	C(13)–C(12)–C(14)	110.3(8)
C(11)–Re(1)–CNT	118.2	P(1)–Re(1)–CNT	125.9
N(1)–Re(1)–CNT	122.8		

[a] CNT, centroid of C_5Me_5 ring.

initially generated, followed by cleavage of the C(1)–C(2) bond of the β-oxoacyl ligand to give **24**.

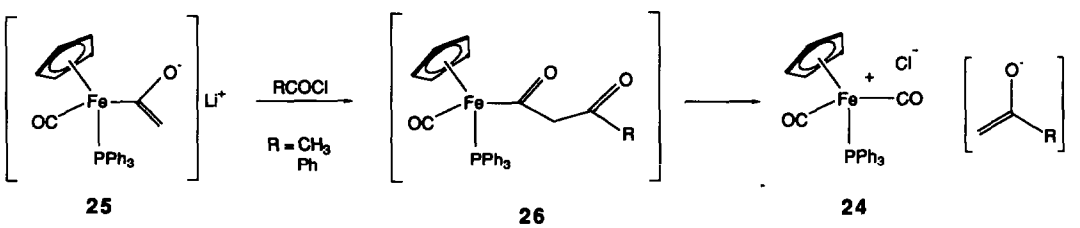
In related work, Davies found that treatment of enolate **25** with acyl halides once again resulted in formation of $[(\eta^5\text{-}C_5H_5)(CO)_2(PPh_3)Fe]^+$ (**24**) and products derived from $RCOCH_2^-$ was indicative of initial formation of **26** followed by spontaneous carbon–carbon bond fragmentation [10].

In contrast to mononuclear β-oxoacyl complexes such as **22** and **26**, the bimetallic μ-malonyl complexes **1**, **2**, and **3** are stable, isolable complexes under neutral conditions. However, in the presence of acid all three bimetallic complexes undergo decomposition to mononuclear species. Not surprisingly, the most stable of the three complexes is the chelating malonyl complex **3**, for which a protonated adduct, **3**-HCl, is reversibly formed and spectroscopically observable. Reaction of anionic malonyl $\{(\eta^5\text{-}C_5Me_5)(NO)(PPh_3)\text{-}Re[\mu\text{-}(COCH_2CO)\text{-}C^1:C^3]Re(CO)_4(Br)\}^-Li^+$ (**1**) with excess HCl resulted in fragmentation of the μ-malonyl ligand by cleavage of either the C(1)–C(2) bond to give **7** and **6** or the C(2)–C(3) bond to give **5** · HCl and $Re(CO)_5Br$ (major products) (Scheme 2). The neutral complex $\{(\eta^5\text{-}C_5Me_5)(NO)(PPh_3)Re[\mu\text{-}(COCH_2CO)\text{-}C^1:C^3]Re(CO)_4(PMe_3)\} \cdot Li^+OTf^-$ (**2**) undergoes a more selective decomposition in the presence of HCl, with cleavage of only the C(1)–C(2) bond of the malonyl ligand to give **7** and **8**-HCl (Scheme 3). In marked contrast, the chelating malonyl complex **3** shows the reverse selectivity in that C(2)–C(3) bond cleavage predominates to give **5**-HCl (Scheme 4). In the absence of further mechanistic information, it is difficult to rationalize this reversal in selectivity.



Scheme 8.

We previously observed the stereoselective incorporation of deuterium into the malonyl ligand of **3** and we have now examined the degree of regio- and stereoselectivity in the alkylation chemistry of **3**. Of the four alkyl halides examined, only methyl iodide gave predominant *C*-alkylation. Allyl bromide, benzyl bromide, and ethyl iodide all led to predominantly *O*-alkylation. This is presumably a steric effect. In the case of methylation the *exo* isomer predominates, the structure of which was verified by X-ray crystallography. Dialkylation also proceeds with a high degree of regio- and stereoselectivity as determined by isotope labelling



Scheme 9.

studies. The observed stereochemistry is readily understood on the basis of electronic and steric rationale described by Gladyzs [1] for similar rhenium systems and by Davies and Liebeskind [7] for related iron systems. Both **11**, and the more sterically crowded dimethyl complex **12**, exhibit ON–Re–C_α–O torsion angles of approximately 180°. In related mononuclear rhenium acyl compounds, extended Huckel MO calculations predict that the ON–Re–C_α–O torsion angle (θ) should be near 0° or 180°. An anti ($\theta = 180°$) conformation has been observed in numerous related rhenium complexes containing an acyl or other unsaturated π-accepter ligand [1], and has been observed in isoelectronic iron acyl compounds (η^5-C_5H_5)(CO)(PPh_3)Fe(COR) [7], as well as in the solid state structures of the μ-malonyl complexes **1**, **2**, and **3** [2a].

Although normally carbon–carbon bonds are kinetically inert, they are easily cleaved in the malonyl systems reported here as well as in the mononuclear β-oxoacyls of Davies. The best analogy may be decarboxylation of organic β-keto acids. The stability of the metal complexed carbon monoxide and carbene fragments generated in these cleavage reactions no doubt provides significant driving force.

4. Experimental section

4.1. General

All manipulations, unless otherwise stated, were performed under purified nitrogen using Schlenk techniques or in a Vacuum Atmospheres nitrogen box equipped with a Dri-Train MO 40-1 purifier and a −29°C freezer. Infrared (IR) spectra were recorded on a Perkin-Elmer 1330 infrared spectrophotometer. Melting points were determined in sealed capillaries on an Electrothermal melting point apparatus equipped with a calibrated thermometer. Mass spectra were performed at the University of California, Riverside Mass Spec (UCRMS) facility. Elemental analyses were performed by Galbraith Laboratories, or Schwarzkopf. ^{1}H, ^{13}C, ^{2}H and ^{31}P NMR spectra were recorded at ambient probe temperature unless otherwise stated on a GE QE 300 NMR spectrometer: ^{1}H, 300 MHz; ^{13}C, 75; ^{2}H, 46; ^{31}P, 121. ^{1}H NMR chemical shifts are reported relative to the residual protio solvent resonance: $CDHCl_2$, δ 5.32; $CHCl_3$, 7.24; THF-d_7, 3.58. ^{13}C NMR chemical shifts are reported relative to the solvent resonance: $CDCl_3$, δ 77.0; CD_2Cl_2, 53.8; THF-d_8, 67.4. ^{2}H NMR chemical shifts are reported relative to $CDCl_3$, δ 7.24. ^{31}P NMR chemical shifts are reported relative to external 85% H_3PO_4 at 23°C. Dried and degassed solvents were used throughout. Electrophiles C_2H_5I, $C_6H_5CH_2Br$, CH_2CHCH_2Br, CD_3I (Aldrich, 99.5 atom % D) and CH_3I were distilled from CaH_2 and manipulated by vacuum transfer. The complexes (η^5-C_5Me_5)(NO)(PPh_3)Re($COCH_3$)[3], [(η^5-C_5Me_5)(NO)(PPh_3)Re(CO)]$^+BF_4^-$ (**7**-BF_4) [5], (η^5-C_5Me_5)(NO)(PPh_3)Re[μ-($COCH_3CO$)-C^1:C^3]Re(CO)$_4$(Br)$^-$-Li^+ (**1**) [2a], (η^5-C_5Me_5)(NO)(PPh_3)Re[μ-($COCH_2$-CO)-C^1:C^3]Re(CO)$_4$(PMe_3) · $Li^+O_3SCF_3^-$ (**2**) [2a], and (η^5-C_5Me_5)(NO)(PPh_3)Re[μ-($COCH_2CO$)-C^1:C^3,O^1]Re(CO)$_4$ (**3**) [2a] were prepared by literature procedures or as previously described.

4.2. Reaction of 1 with HCl

A 5 mm NMR tube was charged with **1** (26 mg, 0.024 mmol, 34 mM) and CH_2Cl_2 (0.7 ml). HCl gas (300 Torr, 0.6 mmol) was then introduced to the yellow slurry at −78°C and the tube was then shaken for 1 min at room temperature. The volatiles were removed under vacuum and the tube was charged with $CDCl_3$, giving a yellow solution with a white precipitate. ^{1}H NMR analysis of the solution indicated a 34:66:66 mixture of [(η^5-C_5Me_5)(NO)(PPh_3)Re=C(OH)CH_3]$^+$ (**5** · HCl) (**7**), and *cis*-(CO)$_4$BrRe=C(OH)CH_3 (**6**). The ^{1}H NMR resonances of these three compounds were identical to those of authentic samples. IR (CH_2Cl_2) spectral analysis of the crude product resulting from a 200 mg scale reaction indicated the additional presence of $(CO)_5ReBr$.

4.3. Reaction of 2 with HCl

A 5 mm NMR tube was charged with **2** (14.9 mg, 0.0123 mmol, 15 mM) and CH_2Cl_2 (0.82 ml). The tube was then exposed to HCl gas at −78°C, warmed to room temperature, and shaken. The volatiles were removed under vacuum and the tube was charged with $CDCl_3$, giving a yellow solution. ^{1}H NMR analysis of this solution indicated formation of **7** and [*cis*-(CO)$_4$(PMe_3)Re=C(OH)CH_3]$^+Cl^-$ (**8** · HCl) in 91% yield. The ^{1}H NMR resonances of **7** and **8** · HCl were identical to those of an authentic sample.

4.4. Reaction of 3 with HCl

A 5 mm NMR tube was charged with **3** (13.4 mg, 0.0136 mmol, 34 mM), $CDCl_3$ (0.4 ml) and cooled to −78°C. HCl gas (0.1 mmol) was added and the tube was then capped with a septum under a stream of nitrogen gas, warmed to room temperature, and shaken. After 20 min, ^{1}H NMR spectral analysis of this solution indicated the presence of (η^5-C_5Me_5)(NO)(PPh_3)-Re[μ-($COCH_2COH$)-C^1,O^3 : C^3]Re(CO)$_4^+Cl^-$ (**3** · HCl) (87%), δ 3.57 (br. s, $\nu_{1/2}$ = 84 Hz, 1H), 2.96 (br. s, $\nu_{1/2}$ = 10 Hz, 1H), 1.77 (s, 15H); **7**(3%); **5** · HCl (13%); and HCl, 5.18 (br.s, $\nu_{1/2} > 100$ Hz). The volatiles were removed under vacuum and $CDCl_3$ was added; ^{1}H NMR analysis indicated recovery of **3** (76%); **5** · HCl (23%); and **7** (~ 1%).

In a related experiment, a 5 mm NMR tube was charged with **3** (13.9 mg, 0.0142 mmol, 36 mM), $CDCl_3$ (0.4 ml) and cooled to −78°C. HCl gas (0.5 mmol) was added and the tube was capped with a septum under a stream of nitrogen gas and allowed to stand overnight. The volatiles were removed under vacuum and $CDCl_3$ was added; ^1H NMR spectral analysis of the solution indicated the presence of a 91:9 mixture of **5** · HCl and **7** in 79% yield and *cis*-$(CO)_4(Cl)Re{=}C(OH)CH_3$ (**10**) (δ 3.02, s, 4%).

In a related experiment, a 5 mm NMR tube was charged with **3** (50 mg, 0.051 mmol, 0.13 M), $CDCl_3$ (0.4 ml), and cooled to −78°C. HCl gas (1.6 mmol) was added and the tube was capped with a septum under a stream of nitrogen gas. The tube was briefly warmed to room temperature and shaken, then placed in a pre-cooled NMR probe: $^{13}C\{^1H\}$ NMR (−40°C): δ 321.7 ($CH_2C(OH)Re(CO)_4$); 286.6 (d, J = 8.8 Hz, (PPh_3)-Re*C*O); 191.3 (Re*C*O); 186.4 (Re*C*O); 185.9 (Re*C*O); 185.4 (Re*C*O); 135.5–128.6 (C_7H_5); 104.3 (C_5Me_5); 88.7 (CH_2); 9.9 (C_5Me_5).

An IR spectrum was obtained of a 4 mM CH_2Cl_2 solution of **3** which had been exposed to HCl gas: 2100m, 2085w, 2045m, 2000 vs, br, 1951 vs, 1923 w, sh, 1667s, 1615w, 1481w, 1391m, 1372m, 1343w cm^{-1}.

4.5. Reaction of 1 with CH_3I

A 5 mm NMR tube was charged with **1** (10 mg, 0.0093 mmol, 19 mM), THF-d_8 (0.5 ml) and CH_3I (0.12 mmol, 0.24 M, by ^1H NMR spectroscopy), and closed under nitrogen gas. After 1 day, ^1H NMR analysis indicated the presence of **1**, ~43%; **11**, ~23%; **12**, <10%; in addition to several unidentified products.

4.6. Preparation of $[(\eta^5\text{-}C_5Me_5)(NO)PPh_3)Re{=}C(OH)CH_3]^+Cl^-$ (5 · HCl)

A round-bottomed flask was charged with **5** (153 mg, 0.233 mmol, 12 mM), diethyl ether (10 ml), and CH_2Cl_2 (10 ml) and then cooled to −78°C. The solution was exposed to HCl gas (0.5 atm) and warmed to room temperature, and then concentrated to *ca.* 10 ml under vacuum. Diethyl ether (10 ml) was then added to the solution and a yellow precipitate was collected by filtration. Recrystallization of this solid from slow addition of hexanes (*ca.* 10 ml) to a CH_2Cl_2 solution yielded **5** · HCl (101 mg, 0.146 mmol, 68%) as a yellow crystalline solid; m.p. 225–227°C (dec). IR (CH_2Cl_2): 1680 cm^{-1}. ^1H NMR ($CDCl_3$): δ 15.59 (br. s, 1H); 7.41–7.33 (m, 15H); 2.38 (s, 3H); 1.73 (s, 15H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 296.6 (d, J = 9.0 Hz, Re=*C*); 133.1 (C_6H_5); 133.0 (C_6H_5); 131.2 (C_6H_5); 128.8 (d, J = 10.8 Hz, C_6H_5); 105.2 (C_5Me_5); 45.4 (CH_3); 9.5 (C_5Me_5). Anal. Found: C, 52.27; H, 5.08; N, 1.97. $C_{30}H_{34}NO_2PReCl$ calcd.: C, 51.98; H, 4.94; N, 2.02%.

4.7. Preparation of $[(CO)_5(PMe_3)Re]^+O_3SCF_3^-$

A round-bottomed flask equipped with a magnetic stirbar was charged with $(CO)_5Re(OSO_2CF_3)$ [11] (1.50 g, 3.16 mmol, 0.11 mM) and CH_2Cl_2 (30 ml). Trimethylphosphine (0.33 ml, 3.19 mmol) was added with rapid stirring. A thick white precipitate formed immediately, and the reaction flask was vigorously shaken for 5 min. Diethyl ether (20 ml) was then added, and a white solid $\{[(CO)_5(PMe_3)Re]^+O_3SCF_3^-\}$ was isolated by filtration (1.65 g, 3.00 mmol, 95%); m.p. 170–179°C (dec). IR (CH_3CN) 2195w, 2049vs, 2020sh, m, 1630w, br, 1298w, 1271s, 1225w, 1155m, 965w cm^{-1}. ^1H NMR (acetone-d_6): δ 2.15 (d, J = 10.9 Hz). MS (FAB): m/e 403 (M^+), 953 ($2M^+OTf^-$). Anal. Found: C, 19.75; H, 1.68. $C_9H_9F_3O_8PReS$ calcd.: C, 19.60; H, 1.64%.

4.8. Preparation of cis-$(CO)_4(PMe_3)Re(COCH_3)$ (8)

A round-bottomed flask equipped with a magnetic stir bar was charged with $[(CO)_5(PMe_3)Re]^+O_3SCF_3^-$ (550 mg, 1.0 mmol, 4 mM) and THF (250 ml), then cooled to 0°C. A 1.5 M solution of CH_3MgBr in toluene/THF (75:25) (0.67 ml, 1.0 mmol) was added and the solution was stirred at 0°C for 0.5 h, then at room temperature for 0.5 h, and then concentrated under vacuum to *ca.* 80 ml. This solution was then filtered through a plug of basic alumina in the air, washing with THF (100 ml). The solvent was removed from the filtrate by rotary evaporation and **8** (220 mg, 53%) was isolated as a yellow oil by chromatography (preparative TLC, silica, CH_2Cl_2/hexanes, 4:3) of the residue. IR (CH_2Cl_2): 2084m, 1990s, sh, 1974vs, 1949s, 1585m cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.43 (s, 3H); 1.63 (d, J = 9.1 Hz, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 257.5 (d, J = 10.9 Hz, Re*O*OCH$_3$); 189.7 (d, J = 10.5 Hz, *cis*-$(PMe_3)ReCO$); 188.7 (d, J = 42.2 Hz, *trans*-$(PMe_3)ReCO$); 188.1 (d, J = 6.0 Hz, *cis*-$(PMe_3)ReCO$); 57.2 (d, J = 2.2 Hz, CH_3); 18.0 (d, J = 34.8 Hz, P*Me*$_3$). Anal. Found: C, 25.82; H, 2.83. $C_9H_{12}O_5PRe$ calcd.: C, 25.90; H, 2.90%.

4.9. Preparation of $[cis\text{-}(CO)_4(PMe_3)Re{=}C(OH)CH_3]^+Cl^-$ (8 · HCl)

A round-bottomed flask equipped with a magnetic stir bar was charged with **8** (110 mg, 0.26 mmol, 0.03 M) and diethyl ether (10 ml), then cooled to −78°C. The solution was exposed to HCl gas (300 Torr, 6 mmol), warmed to room temperature and stirred for 15 min. A white solid (**8** · HCl, 88 mg, 0.19 mmol, 75%) was isolated by filtration: m.p. 66–68°C. IR (CH_2Cl_2): 2104w, 2020m, 2000vs cm^{-1}. ^1H NMR ($CDCl_3$): δ 15.46 (s, 1H); 2.96 (s, 3H); 1.72 (d, J = 9.4 Hz, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 294.2 (br. m, Re=*C*); 186.5 (d, J = 6.9 Hz, *cis*-$(PMe_3)ReCO$); 186.3 (d, J = 10.0 Hz, *cis*-$(PMe_3)ReCO$); 185.1 (d, J = 38.6 Hz, *trans*-

(PMe_3)ReCO); 52.5 (CH_3); 18.4 (d, $J = 35.0$ Hz, PMe_3). Anal. Found: 23.86; H, 2.99. $C_9H_{13}O_5PReCl$ calcd.: C, 23.82; H, 2.89%.

4.10. Preparation of (η^5-C_5Me_5)(NO)(PPh_3)Re[μ-(COCH=$COCH_3$)-C^1,O^3:C^3]Re(CO)$_4$ (14).

A round-bottomed flask equipped with a magnetic stir bar was charged with **3** (101 mg, 0.103 mmol, 7 mM), ^{t}BuOK (13 mg, 0.114 mmol, 8 mM) and THF (15 ml) and stirred for 20 min. Methyl triflate (13 μl, 0.115 mmol, 8 mM) was added and the solution was stirred for 2 h. The solvent was removed under vacuum and the residue was dissolved in CH_2Cl_2 and passed through a plug of silica gel. The solvent was removed from the filtrates by rotary evaporation and the residue was dissolved in hexanes and placed in a 0°C freezer overnight. An orange solid (**14**) was isolated by filtration (42 mg, 0.042 mmol, 41%); m.p. 192–197°C (dec). IR (CH_2Cl_2): 2080m, 1975s, 1913s, 1647s, 1467s cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.4 (br. s, 15H); 6.13 (s, 1H); 3.51 (s, 3H); 1.76 (s, 15H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 271.4 (d, $J = 8.8$ Hz, $PPh_3ReCOCH_2$); 224.4 (ReCOCHMe); 193.4 (ReCO); 193.0 (ReCO); 189.3 (ReCO); 188.8 (ReCO); 134.4 (d, $J = 10.6$ Hz, CH=); 133.9 (br. m, C_6H_5); 130.2 (C_6H_5); 128.2 (C_6H_5); 128.1 (C_6H_5); 103.0 (C_5Me_5); 58.4 (OCH_3); 9.9 (C_5Me_5). MS (FAB): *m/e* 996 (M^+), matched calculated isotopic distribution pattern for $C_{36}H_{34}NO_7PRe_2$. Anal. Found: C, 43.46; H, 3.51; N, 1.39. $C_{36}H_{34}NO_7PRe_2$ calcd.: C, 43.41; H, 3.44; N, 1.41%.

4.11. Preparation of (η^5-C_5Me_5)(NO)(PPh_3)Re[μ-(COCHCH$_3$CO)-C^1, O^3:C^3]Re(CO)$_4$ (11)

A round-bottomed flask equipped with a magnetic stir bar was charged with **3** (310 mg, 0.316 mmol, 9 mM), ^{t}BuOK (49 mg, 0.442 mmol) and THF (35 ml), and was then stirred for 1 h. CH_3I (2 ml, 32 mmol) was added and the solution was stirred for 0.5 h. The volatiles were then removed under vacuum and the residue was dissolved in $CHCl_3$. The cloudy solution was filtered in the air through a fine frit covered with celite. The filtrate was concentrated to an oil by rotary evaporation and then hexanes was added to give a yellow solid (**11**, 286 mg, 0.287 mmol, 91%); m.p. 196–200°C (dec). ^{1}H NMR (CD_2Cl_2): δ 7.48, 7.33 (s, br, 15H); 2.10 (q, $J = 7.95$ Hz, 1H); 1.78 (s, 15H); 1.01 (d, $J = 7.92$ Hz, 3H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 298.8 (d, J(PC) = 7 Hz); 276.5, 195.0, 192.9, 192.7, 191.8, 134.5 (m, br); 131.3, 129.1, 128.9, 104.2, 94.7, 15.4, 10.1. IR (CH_2Cl_2): 2075m, sh, 1962s, 1917s, 1654m, 1602w cm^{-1}. FAB mass spectrum: *m/z* 996 (M^+); Anal. Found: C, 43.29; H, 3.38; N, 1.33. $C_{36}H_{34}NO_7PRe_2$ calcd.: C, 43.41; H, 3.44; N, 1.41%.

4.12. Preparation of (η^5-C_5Me_5)(NO)(PPh_3)Re[μ-(COCHCD_3CO)-C^1,O^3:C^3]Re(CO)$_4$(11-d_3)

This complex was prepared by a procedure analogous to that for the unlabeled complex (**11**). IR (CH_2Cl_2): 2080m, 1975vs, 1930s, 1660m, 1610w cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.41 (br. s, 15H); 2.17 (br. s, $\nu_{1/2} = 4.4$ Hz, 1H); 1.76 (s, 15H). ^{2}H{^{1}H} NMR ($CHCl_3$): δ 1.00 (br. s).

4.13. Preparation of (η^5-C_5Me_5)(NO)(PPh_3)Re{μ-[COC(CH_3)$_2$CO]-C^1,O^3:C^3}Re(CO)$_4$ (12)

A round-bottomed flask was charged with **10** (256 mg, 0.257 mmol, 7 mM), ^{t}BuOK (48 mg, 0.421 mmol, 12 mM) and THF (35 ml) and stirred for 4 h. Methyl iodide (0.75 ml, 2.3 mmol, 66 mM) was added and the solution was stirred for 2 h. The volatiles were removed under vacuum and the residue was dissolved in $CHCl_3$ and then filtered through a frit covered with celite. The solvent was removed from the filtrate and the residue was dissolved in THF. Hexanes was added and a bright yellow solid (**12**) was isolated by filtration (220 mg, 0.218 mmol, 85%); m.p. 192–197°C (dec). IR (CH_2Cl_2): 2078m, 1971vs, 1925s, 1655m, 1600w cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.41 (br. s, 15H); 1.68 (s, 15H); 0.95 (s, 3H); 0.03 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 304.8 (d, $J = 8$ Hz, $PPh_3ReCOCH_2$); 277.8 (Re$COCH_2$); 195.3 (ReCO); 192.4 (ReCO); 191.7 (ReCO); 191.5 (ReCO); 133.8 (C_6H_5); 130.7 (C_6H_5); 128.6 (C_6H_5); 128.5 (C_6H_5); 103.6 (C_5Me_5); 93.1 (CH_2); 23.3 (*endo*-CH_3); 17.7 (*exo*-CH_3); 9.9 (C_5Me_5). MS (FAB: *m/e* 1010 (M^+), matched calcd isotopic distribution pattern for $C_{37}H_{36}NO_7PRe_2$.

4.14. Preparation of (η^5-C_5Me_5)(NO)(PPh_3)Re{μ-[COC(CH_3)(CD_3)CO]-C^1,O^3:C^3}Re(CO)$_4$ (12-endo-d_3)

This complex was prepared by a procedure analogous to that for the unlabeled complex (**12**), employing **11**-d_3; m.p. 207–209°C (dec). ^{1}H NMR ($CDCl_3$): δ 7.41 (br. s, 15H); 1.68 (s, 15H); 0.94 (s, 3H); a very low intensity singlet was observed at δ 0.03. The ratio of intensities of the singlets at δ 0.94 and 0.03 was 83:1. ^{2}H{^{1}H} NMR ($CHCl_3$); δ 0.01 (s).

4.15. Preparation of (η^5-C_5Me_5)(NO)(PPh_3)Re{μ-[COC(CD_3)(CH_3)CO]-C^1,O^3:C^3}Re(CO)$_4$ (12-exo-d_3)

This complex was prepared by a procedure analogous to that for the unlabeled complex (**12**) employing CD_3I; m.p. 205–208°C (dec). ^{1}H NMR ($CDCl_3$): δ 7.41 (br. s, 15H); 1.68 (s, 15H); 0.03 (s, 3H); a very low intensity singlet was observed at δ 0.93. The ratio of intensities of the singlets at δ 0.03 and 0.93 was 65:1. ^{2}H{^{1}H} NMR ($CHCl_3$): δ 0.93 (s).

4.16. Preparation of $(\eta^5\text{-}C_5Me_5)(NO)(PPh_3)Re[\mu\text{-}(COCH{=}COCH_2C_6H_5)\text{-}C^1,O^3:C^3]Re(CO)_4$ ***(18)***

A round-bottomed flask equipped with a magnetic stir bar was charged with **3** (150 mg, 0.153 mmol, 5 mM), ^{t}BuOK (25 mg, 0.219 mmol, 7 mM) and THF (30 ml) and stirred for 0.5 h. Benzyl bromide (2 ml, 20 mmol, 0.7 M) and the solution was stirred overnight and then the volatiles were removed under vacuum. An orange solid (**19**) was isolated by silica gel chromotography in the air, eluting with benzene (124 mg, 0.116 mmol, 76%); m.p. 200–206°C (dec). IR (CH_2Cl_2): 2082m, 1975vs, 1915vs, 1650s, 1470m, 1444m cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.40 (m, 20H); 6.30 (s, 1H); 4.86 (d, $J = 12.4$ Hz, 1H); 4.69 (d, $J = 12.4$ Hz, 1H); 1.74 (s, 15H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 271.3 (d, $J = 9.5$ Hz); 223.9, 193.3, 192.9, 189.3, 188.6, 138.0, 136.0, 133.8 (br. m); 130.2, 128.2, 128.0, 127.2, 127.0, 103.0, 73.3, 9.9. Anal. Found: C, 47.39; H, 3.72; N, 1.19. $C_{42}H_{38}NO_7PRe_2$ calcd.: C, 47.05; H, 3.57; N, 1.31%.

4.17. Preparation of $(\eta^5\text{-}C_5Me_5)(NO)(PPh_3)Re[\mu\text{-}(COCH{=}COCH_2CH_3)\text{-}C^1,O^3:C^3]Re(CO)_4$ ***(16)*** *and* $(\eta^5\text{-}C_5Me_5)(NO)(PPh_3)Re[\mu\text{-}(COCHCH_2CH_3CO)\text{-}C^1,O^3:C^3]Re(CO)_4$ ***(15)***

A round-bottomed flask was charged with **3** (205 mg, 0.209 mmol, 6 mM), ^{t}BuOK (0.263 mmol, 7 mM) and THF (35 ml) and stirred for 1.5 h. Ethyl iodide (1 ml, 13 mmol, 0.4 M) was added and the solution was stirred for 2 h. The volatiles were removed under vacuum and the residue was dissolved in $CHCl_3$ and filtered through a frit covered with celite. ^1H NMR spectroscopy ($CDCl_3$) on the filtrate indicated a 77% and 10% yield of **16** and **15**, respectively. An orange solid (**15**) was isolated by extracting the filtrates with hexanes; m.p. 182–191°C (dec). IR (CH_2Cl_2): 2070m, 1979vs, 1914s, 1645m, 1348m, 1380w cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.37 (br. s, 15H); 3.89 (8 line m, 1H); 3.74 (8 line m, 1H); 1.76 (s, 15H); 1.28 (t, $J = 7.1$ Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 270.4 (d, $J = 9.3$ Hz); 224.4, 193.3, 193.1, 189.5, 188.7, 135.6, 133.8 (br. m); 130.1, 128.1, 128.0, 102.8, 67.8, 9.9, 9.8. MS (FAB): *m/e* 1010 (M^+), matched calculated isotopic distribution pattern for $C_{37}H_{36}NO_7PRe_2$. Anal. Found: C, 43.29; H, 3.70; N, 1.42. $C_{37}H_{36}NO_7PRe_2$ calcd.: C, 43.40; H, 3.59; N, 1.39%. A yellow crystalline solid (12:1 mixture of **16** and **15**) (was isolated by recrystallization of the filtrates (CH_2Cl_2/hexanes) at −30°C; m.p. 200–210°C (dec). IR (CH_2Cl_2): 2078s, 1970vs, 1922vs, 1661s, 1610m, 1393m, 1371m cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.40 (m, 15H); 1.87 (dd, $J = 9.2$, 3.7 Hz, 1H); 1.76 (s, 15H); 1.60 (m, 2H); 0.89 (t, $J = 7.3$ Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 297.9 (d, $J = 8.2$ Hz); 274.3, 194.2, 192.4, 191.4, 190.9, 133.7 (br. m); 130.7, 130.5, 130.2, 128.2, 128.1, 103.3, 100.1, 22.1, 11.7, 9.4. Anal. $C_{37}H_{36}NO_7PRe_2$ calcd.: Found: C, 43.10; H, 3.59; N, 1.23. C, 43.40; H, 3.59; N, 1.39%.

4.18. Preparation of $(\eta^5\text{-}C_5Me_5)(NO)(PPh_3)Re[\mu\text{-}(COCCH_3{=}COCH_2CH_3)\text{-}C^1,O^3:C^3]Re(CO)_4$ ***(21)***

A round-bottomed flask equipped with a magnetic stir bar was charged with **11** (147 mg, 0.148 mmol, 7 mM), ^{t}BuOK (26 mg, 0.232 mmol, 12 mM) and THF (20 ml) and then stirred for 3 h. Ethyl iodide (1 ml, 12 mmol, 0.6 M) was added and the solution was stirred for 3 h. The volatiles were removed under vacuum and the residue was chromatographed on a silica gel column in the air eluting with 1:1 CH_2Cl_2/hexanes. The solvent was removed by rotary evaporation to give an orange solid (**21**, 127 mg, 0.124 mmol, 84%); m.p. 157–163°C (dec). ^1H NMR ($CDCl_3$): δ 7.40 (m, 15H); 4.13 (m, 2H); 2.01 (s, 3H); 1.74 (s, 15H); 1.33 (t, $J = 7.0$ Hz, 3H). $^{13}C\{^1H\}$ NMR: δ 276.7 (d, $J = 9.5$ Hz); 222.0, 193.9, 193.1, 198.3, 186.9, 144.3, 133.6 (br. m); 130.1, 128.1, 128.0, 102.1, 74.1, 15.9, 13.2, 9.8. Anal. Found: C, 44.70; H, 3.95; N, 1.43. $C_{38}H_{38}NO_7PRe_2$ calcd.: C, 44.57; H, 3.74; N, 1.37%.

4.19. Preparation of $(\eta^5\text{-}C_5Me_5)(NO)(PPh_3)Re[\mu\text{-}(COCCH_3{=}COCH_3)\text{-}C^1,O^3:C^3]Re(CO)_4$ ***(20)***

A round-bottomed flask equipped with a magnetic stir bar was charged with **11** (30 mg, 0.030 mmol, 3 mM), ^{t}BuOK (4.6 mg, 0.041 mmol, 4 mM), THF (10 ml), and was then stirred for 0.5 h. $Me_3O^+BF_4^-$ (6.5 mg, 0.044 mmol, 4 mM) was added and the mixture was stirred for 12 h. The volatiles were removed under vacuum and the residue was chromatographed on a column of silica gel in the air eluting with 2:3 CH_2Cl_2/hexanes. The solvent was removed by rotary evaporation to give an orange solid (**20**, 13 mg, 0.013 mmol, 43%). IR (CH_2Cl_2) 2085m, 1984vs, 1912s, 1640m, 1477m, 1408w cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.40 (br. s, 15H); 3.89 (s, 3H); 1.98 (s, 3H); 1.72 (s, 15H). $^{13}C\{^1H\}$ NMR: δ 277.5 (d, $J = 9.0$ Hz); 223.2, 193.9, 193.1, 189.1, 186.6, 144.8, 134.0 (br. m); 130.2, 128.2, 128.0, 127.9, 102.2, 65.9, 12.9, 9.8. MS (FAB): *m/e* 1010 (M^+), matched calculated isotopic distribution pattern for $C_{37}H_{36}NO_7PRe_2$.

4.20. Preparation of $(\eta^5\text{-}C_5Me_5)(NO)(PPh_3)Re\{\mu\text{-}[COCH{=}C(OCH_2CH{=}CH_2)]\text{-}C^1,O^3:C^3\}Re(CO)_4$ ***(18)*** *and* $(\eta^5\text{-}C_5Me_5)(NO)(PPh_3)Re\{\mu\text{-}[COCH(CH_2\text{-}CH{=}CH_2)CO]\text{-}C^1:C^3,O^3\}Re(CO)_4$ ***(17)***

These complexes were prepared following a procedure analogous to the above preparations, employing **3** and allyl bromide. ^1H NMR spectral analysis of the crude reaction material indicated formation of **18** and **17** in 57% and 27% yields, respectively. Complex **18** was isolated by silica gel chromotography followed by

recrystallization as an orange solid (15%); m.p. 162–164°C (dec). IR (CH_2Cl_2): 2081m, 1979vs, 1918s, 1649m, 1469m, 1448m, 1311w cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.37 (br. s, 15H); 6.23 (s, 1H); 5.95 (m, 1H); 5.28 (dd, $J = 17.6$, 1.0 Hz, 1H); 5.17 (d, $J = 10.4$ Hz, 1H); 4.34 (dd, $J = 13.4$, 4.9 Hz, 1H); 4.18 (dd, $J = 13.4$, 4.9 Hz, 1H); 1.74 (s, 15H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 271.1 (d, $J = 9.5$ Hz); 270.9, 224.1, 193.3, 193.0, 189.4, 188.6, 135.9, 134.1, 133.7 (d, $J = 10.2$ Hz); 130.2, 128.2, 128.1, 116.5, 102.9, 72.6, 9.9. HRMS (FAB): *m/e* calculated, 1021.1317; found, 1021.1361. Anal. Found: C, 44.70; H, 3.45. $C_{38}H_{36}NO_7PRe_2$ calcd.: C, 44.65; H, 3.56%.

4.21. X-Ray crystal structure determinations for $(\eta^5\text{-}C_5Me_5)(NO)(PPh_3)Re\{\mu\text{-}[COCHCH_3CO]\text{-}C^1, O^3\text{:}C^3\}Re(CO)_4$ *(11) and* $(\eta^5\text{-}C_5Me_5)(NO)(PPh_3)Re\{\mu\text{-}[COC(CH_3)_2CO]\text{-}C^1,O^3\text{:}C^3\}Re(CO)_4$ *(12)*

X-Ray data were collected on a Nicolet R3m/V automated diffractometer system with a dedicated Micro VAX II computer system. Parameters for both structures are summarized in Table 2. The structure of **11** was solved by heavy-atom methods. All non-hydrogen atoms were refined anisotropically, all hydrogen atoms idealized, and the phenyl rings were constrained to rigid hexagons. All computations were carried out using SHELTXTL PLUS software (Nicolet XRD, Madison, WI).

The structure of **12** was solved by direct methods using the full-matrix least-squares refinement method. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were included in idealized positions. There was no evidence of secondary extinction. All computations were carried out using SHELTXTL PLUS software (Nicolet XRD, Madison, WI).

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8 For correspondence concerning the crystallographic details of **11** contact author A.L.R.
9 For correspondence concerning the crystallographic details of **12** contact author R.K.C. at Department of Chemistry, The Scripps Research Institute, 10666 North Torrey Pines Road, La Jolla, CA 92037, USA.
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