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2-Cyclopropene-1-carbonyl Compounds of Rhenium, Manganese, and Iron. A Facile Route to Nonfluxional 3-η^1-Cyclopropenyl Compounds of Rhenium

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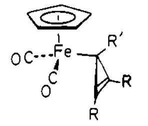
Abstract: 2,3-Diphenyl-2-cyclopropene-1-carbonyl chloride reacts with $[Re(CO)_5]^-$, $[Mn(CO)_5]^-$, and $[Fe(\eta\text{-}C_5H_5)(CO)_2]^-$ to give the acyl compounds **2**, **10**, and **11**, respectively. Similarly 2-*tert*-butyl-2-cyclopropene-1-carbonyl chloride and 2-*tert*-butyl-3-deuterio-2-cyclopropene-1-carbonyl chloride react with $[Re(CO)_5]^-$ to give the rhenium acyls **5** and **7**, respectively. The rhenium acyls **2**, **5**, and **7** undergo a mild thermal decarbonylation reaction which proceeds with allylic rearrangement of the migrating cyclopropenyl group to give the (3-η^1-cyclopropenyl)rhenium compounds **3**, **6**, and **8**, respectively. Compound **8** is inert to ring-whizzing of the $Re(CO)_5$ moiety at 63 °C, allowing a minimum activation energy of 32 kcal·mol^{-1} to be calculated for such a process. The manganese acyl **10** also undergoes decarbonylation, but only $[Mn_2(CO)_{10}]$ and a tetraphenylbenzene can be isolated. The iron acyl **11** could not be decarbonylated thermally.

Allyl and substituted allyl ligands are ubiquitous in organometallic chemistry; examples of η^3-, η^1-, and μ-allylic ligands abound and their chemistry have been well established. Examples of cyclopropenyl transition-metal compounds, containing the cyclic analogue of the allyl ligand, are relatively rare. The only compounds characterized to date in the which a symmetrical η^3-coordination mode for a cyclopropenyl ligand has been reported are $[NiBr(CO)(\eta\text{-}C_3R_3)]$ (R = Ph,[2,3] *t*-Bu[3]), $[NiBr(\eta^3\text{-}C_3\text{-}t\text{-}Bu_3)]_2$,[3] $[NiBrL_2(\eta\text{-}C_3Ph_3)]$ (L = CO, py),[2-4] $[Ni(\eta\text{-}C_5H_5)(\eta^3\text{-}C_3R_3)]$ (R = Ph,[4] *t*-Bu[3]), $[Co(CO)_3(\eta\text{-}C_3Ph_3)]$,[5] $[MoBr(CO)_2L_2(\eta\text{-}C_3Ph_3)]$ (L = MeCN,[6,7] L_2 = 2,2′-bipyridyl,[7] 1,10-phenanthroline[7]), and $[Mo(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_3Ph_3)]$.[6] Unsymmetrically bound cyclopropenyl ligands have been characterized in the cations $[M(PPh_3)_2(\eta^2\text{-}C_3Ph_3)]^+$ (M = Ni, Pd, Pt).[8-10] A number of compounds derived from C–C bond cleavage reactions have also been prepared. This latter topic is discussed in the following paper[11] and has also been the subject of a theoretical investigation.[12] In all cases, the synthetic approach to the cyclopropenyl compound has involved reactions of cyclopropenium cations with nucleophilic metal centers.

3-η^1-Cyclopropenyl ligands are even rarer, and only one class of compound containing such ligands had been characterized prior to our work. The reaction of the $[Fe(CO)_2(\eta\text{-}C_5H_5)]^-$ anion with various cyclopropenium cations was reported to yield compounds **1**,[13,14] and the structure of **1a** was confirmed crystallographically.[14]

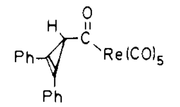


1a. R = R′ = Ph.
1b. R = Ph, R′ = H.
1c. R = ^{t}Bu, R′ = Me.

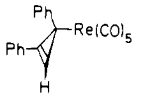
This paper describes a new synthesis of (3-η^1-cyclopropenyl)rhenium compounds, and the synthesis of 2-cyclopropene-1-carbonyl compounds of rhenium, manganese, and iron. The principal motivation for this study was to develop a synthetic method for selectively generating deuterium-labeled 2-cyclopropenyl compounds, in order to examine the facility with which they might undergo the fluxional reaction commonly referred to as ring-whizzing.[15] A preliminary account of some of these findings has appeared.[16]

Results

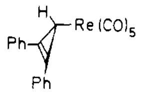
The reaction of 2,3-diphenyl-2-cyclopropene-1-carbonyl chloride with $Na^+[Re(CO)_5]^-$ in THF solution at −78 °C yielded the rhenium acyl compound **2**; this compound proved to be surprisingly labile in THF solution at temperatures exceeding −20 °C and could only be isolated in pure form by evaporation of the THF at −20 °C followed by extraction of **2** at 20 °C into a nonpolar solvent. The IR and mass spectrum of **2** clearly established it as an acylpentacarbonylrhenium compound. The ^{13}C NMR spectrum of **2** showed the presence of a single type of phenyl group and a single resonance for the two olefinic carbon atoms, unambiguously defining the structure of **2** as shown, with a plane of symmetry bisecting the cyclopropene ring. The ^1H NMR spectrum of **2** showed a singlet resonance at δ 2.98 together with phenyl resonances.



2.



3.



4.

When **2** was left standing in THF or $CDCl_3$ solution at 20–25 °C, it underwent a clean, quantitative thermal decarbonylation reaction to afford a single product, characterized by its IR and mass spectrum as a pentacarbonylrhenium compound. In contrast to its immediate precursor **2**, this compound exhibited no ^1H NMR resonances at high field, characteristic of protons attached to the saturated carbon of a cyclopropene, but instead showed a singlet resonance at δ 6.43, characteristic of a vinylic cyclopropene proton,

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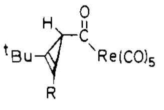
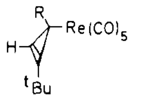
together with phenyl resonances. The ^{13}C NMR spectrum clearly indicated that the two phenyl rings were nonequivalent, as were the two olefinic carbon atoms of the cyclopropene. These data can only be reconciled with structure **3** and not with the expected product **4**. Attempts to induce migration of the cyclopropenyl ligand back on to CO, by prolonged refluxing of solutions of **3** with PPh_3, effected no such conversion, and **3** could be recovered unchanged.

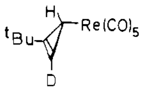
The acyl complex **5** was synthesized from the appropriate acyl chloride precursor at low temperatures, as described above. The ^{1}H NMR spectrum of **5** exhibited a singlet *t*-Bu resonance at δ 1.15, a saturated cyclopropene proton resonance at δ 2.92 (d, J = 1.2 Hz), and a vinylic resonance at δ 6.18 (d, J = 1.2 Hz), clearly consistent with the illustrated structure. This molecule was even more labile than **2** toward decarbonylation and rapidly afforded a single product **6**, whose structure was unambiguously characterized by its ^{1}H NMR spectrum. A singlet *t*-Bu resonance (δ 1.20) together with two doublets (J = 1.2Hz) at δ 2.20 and 6.20 can only be interpreted in terms of structure **6**. An analogous procedure yielded first the specifically deuterium-labeled acyl **7**, whose ^{1}H NMR spectrum exhibited only a singlet *t*-Bu resonance (δ 1.15) and a *singlet* at δ 2.92 (cf. **5**). This compound decarbonylated smoothly at 20 °C to give **8** as the sole product; **8** exhibited singlet ^{1}H NMR peaks at δ 1.15 (*t*-Bu) and 6.20 (vinylic cyclopropene proton), but no resonance at δ 2.20 (cf. **6**). The absence of this latter resonance was taken as conclusive evidence that a negligible amount of the isomeric compound **9** was produced during the decarbonylation of **7**.



5. R = H.
7. R = D.



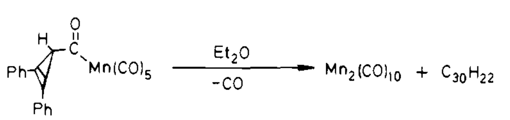
6. R = H.
8. R = D.



9.

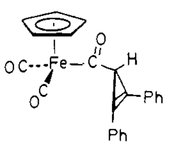
The 3-η^1-cyclopropenyl compounds **3**, **6**, and **8** were moderately stable in chlorinated solvents under N_2 but did decompose slowly at 20–25 °C to give $[Re(CO)_5Cl]$ and unidentified organic products. Compound **8** could be recovered unchanged after 6 h in C_6D_6 solution at 63 °C but decomposed slowly in refluxing C_6D_6 to give $[Re_2(CO)_{10}]$. Under the former set of conditions, assuming <1% conversion of **8** to **9** over a 6-h period, a minimum activation energy of 32 kcal·mol^{-1} for the conversion of **8** to **9** was calculated.[17]

Attempts to extend this chemistry to the corresponding manganese systems met with mixed results. 2,3-Diphenyl-2-cyclopropene-1-carbonyl chloride reacted with $[Mn(CO)_5]^-$ to afford the corresponding acyl compound **10**. This was moderately stable in benzene solution but decomposed in $CDCl_3$ or Et_2O to produce $[Mn_2(CO)_{10}]$ as the only carbonyl-containing compound, together with a crystalline hydrocarbon, identified by its mass spectrum and melting point as 1,2,4,5-tetraphenylbenzene. No evidence for a (3-η^1-cyclopropenyl)manganese compound analogous to **4** could be obtained by either IR or ^{1}H NMR monitoring of this decomposition reaction.



10.

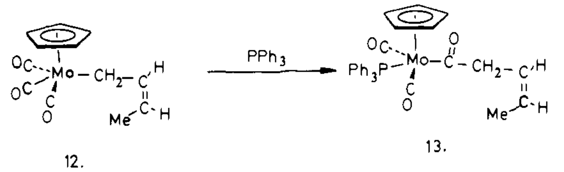
Reaction of the same acid chloride with $[Fe(CO)_2(\eta\text{-}C_5H_5)]^-$ afforded the thermally stable acyl complex **11**,[19] which could be recovered unchanged from refluxing THF or benzene solutions. No thermal decarbonylation of **11** to give analogues of **1** was observed. ^{13}C NMR data for **10** and **11** were also entirely compatible with those obtained for **2**.



11.

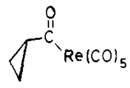
Discussion

The migration of alkyl ligands to and from an adjacent CO ligand is a reaction of fundamental importance in organometallic chemistry and in many homogeneously catalyzed organic reactions.[21,22] In every reaction of this type which has been reported to date, the migration involves a 1,2 shift of the alkyl group. In a particularly relevant example the migration of the 2-alkenyl ligand from Mo to CO in the conversion of **12** to **13** has been shown to involve a simple 1,2 shift of the carbon originally bound to the metal, without an allylic rearrangement involving participation of the double bond.[24] Although the reverse reaction has not been investigated, the principle of microscopic reversibility requires that it should also involve a 1,2 shift from CO to the metal.



12. 13.

In light of these results, the observed decarbonylation reaction of **2** to give only **3** was particularly intriguing for two reasons: first, the reaction proceeds under mild thermal conditions, in marked contrast to compound **14**, which is reported to be thermally and photochemically inert toward cyclopropyl migration,[25,26] and second, it does not produce the expected product **4**. The first step was assumed to involve dissociation of a CO ligand to afford a coordinatively unsaturated acyltetracarbonylrhenium intermediate.[21] Following this step we considered, a priori, three possible routes to give **3**: (a) heterolytic dissociation of the acyltetracarbonylrhenium compound to give a cyclopropenium cation and $[Re(CO)_5]^-$,[28] followed by recombination to give **3**, (b) a conventional[21] 1,2 shift of the cyclopropenyl group from CO to Re, giving **4** as the kinetic product, followed by a 1,2 shift of $Re(CO)_5$[29]



14.

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[17] Calculated from d[**9**]/dt = A exp($-E_a/RT$) by using a value of A = 2.84 × 10^{14} calculated from the activation parameters for the dynamic rearrangement of $[Re(\eta^1\text{-}C_7H_7)(CO)_5]$.[18]

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[22] For the purpose of this paper, we have assumed that migration of the organic group occurs. A recent paper[23] does raise anew the possibility of direct CO insertion into a metal–carbon bond as a viable reaction pathway in other systems.

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[28] Heterolytic dissociation of this type has been shown to be an important equilibrium reaction of coordinatively unsaturated acyltricarbonylcobalt compounds in THF solution.[11]

[29] Relatively facile ring-whizzing via 1,2 shifts has been observed for $[Re(CO)(NO)(PMe_3)_2(CH_3)(\eta^1\text{-}C_5H_5)]$[30] and $[Re(CO)_5(\eta^1\text{-}C_7H_7)]$.[18]

around the cyclopropenyl ring to give **3**, and (c) a cyclopropenyl migration with allylic rearrangement to afford **3** in a single step.

While literature precedents favor paths a or b, our experimental observation of clean decarbonylation of **7** to give *only* **8**, clearly eliminates both these pathways; path a should produce a 1:1 mixture of **8**/**9** while path b should afford **9** initially, followed by equilibration of **9** with **8**. The transfer of the cyclopropenyl group from CO to Re can only occur with allylic rearrangement of the migrating group to the exclusion of a 1,2 shift; the importance of the cyclopropene olefin in facilitating this migration is emphasized by the thermal inertness of **14**. This represents the first characterization of such a reaction.[31] It is also notable, though perhaps not unexpected, that the conversion of **7** to **8** (and **5** to **6**) is regiospecific, with Re bonding to the less hindered carbon atom of the olefin. We also note that the comparatively large steric effect on Re–C bond formation which must be encountered in the direct formation of **3** from **2** does not appear to raise the activation energy for the allylic rearrangement pathway sufficiently for a 1,2 shift to become competitive. However, the qualitative difference in the rate of conversion of **2** to **3** as compared to that of **5** to **6** probably does reflect the availability of an unsubstituted olefinic site in the latter case.

The failure to induce cyclopropenyl migration back to CO by treatment of **3** with PPh_3 is not surprising. The inertness of $[Re(CO)_5(CH_3)]$ toward alkyl migration has been noted, even at 140 °C and 320 atm of CO.[32] The only reported example of alkyl migration to CO in a Re complex involves an $AlBr_3$-induced expansion of the strained ring in $[\overline{ReCH_2CMe_2CH_2OPR_2}(CO)_4]$.[33]

The nonconversion of **8** to its isomer **9** by a degenerate ring-whizzing rearrangement is notable in view of the facility with which such rearrangements occur in η^1-C_5H_5 metal complexes.[15,30,34] The activation energies for ring-whizzing in η^1-C_5H_5 metal compounds usually lie in the range of 8–11 kcal·mol^{-1},[15] whereas we have calculated a minimum value of 32 kcal·mol^{-1} for the intramolecular conversion of **8** to **9**. The difference in these activation energies can be reconciled by the realization that ring-whizzing in η^1-C_5H_5 compounds may involve an orbital symmetry allowed [1,5]-sigmatropic shift of the migrating group, whereas the corresponding rearrangement in a η^1-cyclopropenyl compound would involve a forbidden [1,3]-sigmatropic shift,[34,35] assuming that the metal orbital involved in the migration is isolobal with a methyl group. Theoretical calculations on a flat, square-pyramidal $Mn(CO)_5$ group[36] indicate that this isolobal analogy should be true for **8**. Also in agreement with this idea is the observation that ring-whizzing in η^1-C_5H_5 compounds of silicon[37] and iron[38] involves [1,5]-sigmatropic shifts which occur with retention of configuration at the migrating center. We also note that the activation energy for the [1,3]-sigmatropic shift of a Me_3Si group in the interconversions of cyclopropenes **15a** and **15b**, has been observed experimentally to be ca. 31–33 kcal·mol^{-1},[39] a value remarkably similar to the minimum value calculated for **8**. We have noted previously[16] that the compound $[Re(CO)_5(\eta^1\text{-}C_7H_7)]$[18] exhiibits an activation energy (19.8 kcal·mol^{-1}) for an apparent [1,7]-sigmatropic shift of $Re(CO)_5$ which is intermediate between η^1-C_5H_5 and η^1-C_3H_3 systems as expected.[53] More recent results indicate that $[Re(\eta\text{-}C_5H_5)(\eta^1\text{-}C_7H_7)(CO)(NO)]$ is nonfluxional on the ^1H NMR time scale at 130 °C, and that the chiral Re center is also configurationally stable at this temperature.[40] The reasons for the different activation energies for the two η^1-C_7H_7 compounds of Re are unclear, as is the explanation of why $[Sn(\eta^1\text{-}C_7H_7)Ph_3]$ undergoes a [1,5] rather than a [1,7] shift of the metal center.[41,42] Adding to this rather confusing situation is the recent observation that the metal in $[Ru(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_7H_7)(CO)_2]$ undergoes both [1,7] and [1,5] shifts around the cycloheptatrienyl ring; in this case the [1,7] shift is of lower energy than the [1,5].[55] Finally, we note that the nonfluxional behavior of **8** contrasts with the rapid ring-whizzing around the η^2-cyclopropenyl ligand in $[M(PPh_3)_2(C_3Ph_3)]^+$ (M = Ni, Pd, Pt).[10]

15a. 15b.

We have been unable to prepare analogous η^1-cyclopropenyl compounds of manganese. The acyl complex **10** does decarbonylate under the same conditions as its Re analogue **2**, but only $[Mn_2(CO)_{10}]$ and 1,2,4,5-tetraphenylbenzene can be observed as products. The reaction of $[Mn(CO)_5]^-$ with the triphenylcyclopropenium cation has been shown to give only $[Mn_2(CO)_{10}]$ and $(C_3Ph_3)_2$.[3,43] It seems reasonable to suppose that both these reactions give initially an unstable (η^1-cyclopropenyl)manganese analogue of **3** but that the weaker Mn–C bond[44] leads to homolysis and subsequent radical coupling.[43] The same trend in metal–carbon bond stability has been assumed for the corresponding η^1-C_7H_7 systems; $[Re(CO)_5(\eta^1\text{-}C_7H_7)]$ can be isolated and characterized,[18] but attempts to prepare the manganese analogue by decarbonylation of $[Mn(COC_7H_7)(CO)_5]$[45] or by the reaction of $[Mn(CO)_5]^-$ with the tropylium cation[45,46] lead only to $[Mn(\eta^5\text{-}C_7H_7)(CO)_3]$[45] or to $[Mn_2(CO)_{10}]$ and ditropyl.[45,46] An alternative explanation could involve single-electron-transfer reactions between $[Mn(CO)_5]^-$ and the organic cation. Notably reduction of the 1,2-diphenylcyclopropenium cation with Zn or Li/Hg does lead to 1,2,4,5-tetraphenylbenzene via a bicyclopropenyl intermediate.[52] The thermal stability of the iron acyl **11** toward decarbonylation is not surprising, in view of similar observations for acyl complexes of this type.[21]

Finally, it must be noted that the decarbonylation of the rhenium acyl complexes **2**, **5**, and **7** to give exclusively η^1-cyclopropenyl compounds stands in clear contrast to the decarbonylation reactions of ((2-cyclopropene-1-yl)carbonyl)tetracarbonylcobalt compounds, which yield only (η^3-cyclobutenonyl)cobalt complexes upon decarbonylation.[11,20] No evidence for reversible migration of the cyclopropenyl group from CO to cobalt has been obtained for these latter systems,[11] and the reasons for the different chemistries of the Re and Co compounds remain unclear.

Experimental Section

General Data. All reactions were run under an atmosphere of dry nitrogen. Solvents were dried by distillation from sodium benzophenone ketyl, except for CH_2Cl_2 and $CDCl_3$, which were distilled from P_4O_{10}.

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(31) Allylic rearrangements during the "insertion" of SO_2 into allylic metal bonds have been well documented, but this reaction appears to proceed via an electrophilic attack of SO_2 on the allylic ligand and is not mechanistically comparable to our system. For a review of SO_2 "insertion" reactions, see: Wojcicki, A. *Adv. Organomet. Chem.* **1974**, *12*, 31–81. See also: Hartman, F. A.; Pollick, P. J.; Downs, R. L.; Wojcicki, A. *J. Am. Chem. Soc.* **1967**, *89*, 2493–2495.

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IR spectra were run on a Perkin-Elmer PE 257 instrument and were calibrated by using the 1601-cm^{-1} peak of polystyrene. ^{1}H NMR spectra (60 MHz) and ^{13}C{^{1}H} NMR spectra (15 MHz) were run on a JEOL FX-60Q spectrometer; chemical shifts are reported in parts per million downfield from internal Me_4Si. Mass spectra were run on a Finnegan 4023 GC/mass spectrometer. Microanalyses were run by Spang, Eagle Harbor, MI, or by Atlantic Microlab., Atlanta, GA.

Decacarbonyldirhenium, decacarbonyldimanganese, and bis(η-cyclopentadienyl)tetracarbonyldiiron were obtained from the Pressure Chemical Co. 2,3-Diphenyl-2-cyclopropene-1-carbonyl chloride,[47,48] 2-*tert*-butyl-2-cyclopropene-1-carbonyl chloride,[11,49,50] and 2-*tert*-butyl-3-deuterio-2-cyclopropene-1-carbonyl chloride[11,51] were prepared by literature procedures.

((2,3-Diphenyl-2-cyclopropen-1-yl)carbonyl)pentacarbonylrhenium (2). A solution of $[Re_2(CO)_{10}]$ (1.00 g, 1.5 mmol) in THF (15 mL) was reduced by stirring over an amalgam of Na (0.25 g, 10.9 mmol) in Hg (15 mL) for 1 h at 0 °C. Excess amalgam was removed, and the red-orange solution of $[Re(CO)_5]^-$ was filtered under N_2 and cooled to −78 °C. A solution of 2,3-diphenyl-2-cyclopropene-1-carbonyl chloride (0.79 g, 3.1 mmol) in THF (10 mL) was added dropwise, and the resultant yellow solution was stirred at −78 °C for 2 h. The THF was then removed under vacuum, taking care that the temperature of the solution did not rise above −20 °C. The resultant yellow residue was extracted with a mixture of hexanes (10 mL) and toluene (5 mL); the extracts were filtered and set aside at −30 °C overnight to afford **2** as yellow crystals: 0.48 g, 29%; mp 92–94 °C; IR (hexane) ν_{CO} 2122 (w), 2054 (w), 2009 (s), 1984 (s), 1592 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.98 (s, CH), 7.37–7.72 (m, Ph); ^{13}C NMR (C_6D_6) δ 255.69 (C=O), 184.64 (C≡O), 131.12, 130.10, 129.62, 128.76 (Ph), 114.52 (=CPh), 55.03 (CH); mass spectrum (using ^{187}Re), *m/e* 546 (P^+), 518 ($P^+ - CO$), 462 ($P^+ - 3CO$), 434 ($P^+ - 4CO$), 406 ($P^+ - 5CO$), 378 ($P^+ - 6CO$), 191 (C_3Ph_2H). Anal. C, H.

(3-η^1-2,3-Diphenylcyclopropenyl)pentacarbonylrhenium (3). The acyl complex **2** (0.48 g, 0.88 mmol) was dissolved in $CDCl_3$ (3 mL) and allowed to stand at 20 °C. After 4 h, ^{1}H NMR spectroscopy indicated that the δ 2.98 resonance of **2** had completed disappeared and had been replaced by a sharp singlet at δ 6.43. ^{1}H NMR monitoring at intermediate stages revealed no other transient peaks. The solution was evaporated to dryness and chromatographed on a 15 × 1 cm silica gel/hexanes column. Elution with hexanes yielded traces of $[Re_2(CO)_{10}]$ and subsequent elution with benzene afforded a yellow band which yielded an orange oil on evaporation. Repeated recrystallization from hexanes gave **3** as yellow crystals: 0.23 g, 51%; mp 100–103 °C; IR (hexanes) ν_{CO} 2137 (w), 2045 (w), 2025 (vs), 1993 (s), $\nu_{C=C}$ 1730 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.43 (s, C=CH), 6.98–7.61 (m, Ph); ^{13}C NMR ($CDCl_3$) δ 181.86 (C≡O, trans), 180.80 (C≡O, cis), 153.07 (PhC=C), 125.28 (C=CH), 135.32, 132.07, 129.30, 128.50, 128.33, 128.11, 126.45, 123.76 (Ph), the ReCPh resonance could not be observed; mass spectrum (using ^{187}Re), *m/e* 518 (P^+), 462 ($P^+ - 2CO$) 434 ($P^+ - 3CO$), 406 ($P^+ - 4CO$), 378 ($P^+ - 5CO$), 191 (C_3Ph_2H). Anal. C, H.

((3-η^1-1-*tert*-Butylcyclopropen-1-yl)carbonyl)pentacarbonylrhenium (5). A solution of $Na[Re(CO)_5]$ (3.0 mmol) in THF (15 mL) was prepared as described above and and cooled to −78 °C. A solution of 2-*tert*-butyl-2-cyclopropene-1-carbonyl chloride (0.49 g, 3.1 mmol) in THF (5 mL) was added dropwise. The reaction mixture swiftly turned yellow, and the solvent was removed under vacuum while the system was maintained at −45 °C by using a $MeCN/N_2$ (liquid) slush bath. The residue was extracted with benzene (10 mL), and the extracts were filtered and evaporated to afford **5** as a yellow oily solid: 0.80 g, 57%; IR (hexanes) ν_{CO} 2123 (w), 2043 (w), 2011 (vs), 1992 (s), 1592 (m), $\nu_{C=C}$ 1725 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.18 (d, *J* = 1.2 Hz, C=CH), 2.92 (d, *J* = 1.2 Hz, CH), 1.15 (s, CMe_3); mass spectrum (using ^{187}Re), *m/e* 450 (P^+), 422 ($P^+ - CO$), 366 ($P^+ - 3CO$), 338 ($P^+ - 4CO$), 310 ($P^+ - 5CO$), 95 (C_3H_2-*t*-Bu). Anal. C, H.

((2-*tert*-Butyl-3-deuterio-2-cyclopropen-1-yl)carbonyl)pentacarbonylrhenium (7) was prepared in identical fashion from $Na[Re(CO)_5]$ (3.0 mmol) and the acid chloride (3.0 mmol) and was isolated as a yellow oily solid: 0.95 g, 68%; IR (hexanes) identical with that of 6; ^{1}H NMR ($CDCl_3$) δ 2.92 (s, CH), 1.15 (s, CMe_3); mass spectrum (using ^{187}Re) *m/e* 451 (P^+), 423 ($P^+ - CO$), 395 ($P^+ - 2CO$), 367 ($P^+ - 3CO$), 339 ($P^+ - 4CO$), 311 ($P^+ - 5CO$), 283 ($P^+ - 6CO$), 96 (C_3HD-*t*-Bu). Anal. C, H.

(3-η^1-1-*tert*-Butylcyclopropenyl)pentacarbonylrhenium (6). A solution of compound **5** (0.40 g, 0.88 mmol) in $CDCl_3$ (3 mL) was allowed to stand at 20 °C for 2 h, at which time ^{1}H NMR spectroscopy indicated complete conversion of **5** to **6**. Evaporation of the solution gave **6** as a pale yellow oil which could not be crystallized: 0.35 g, 94%; IR (hexanes) ν_{CO} 2137 (w), 2042 (w), 2026 (vs), 1988 (s), $\nu_{C=C}$ 1723 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.20 (d, *J* = 1.2 Hz, C=CH), 2.20 (d, *J* = 1.2 Hz, CH), 1.20 (s, CMe_3); ^{13}C NMR ($CDCl_3$) δ 182.01 (C≡O, trans), 181.07 (C≡O, cis), 149.30 (C=*C*-*t*-Bu), 124.26 (C=*C*H), 30.96 (C*Me*$_3$), 29.54 (*C*Me$_3$), 27.88 (Re*C*H); mass spectrum (using ^{187}Re) *m/e* 422 (P^+), 366 ($P^+ - 2CO$), 338 ($P^+ - 3CO$), 310 ($P^+ - 4CO$), 282 ($P^+ - 5CO$). Anal. C, H.

(3-η^1-1-*tert*-Butyl-2-deuteriocyclopropenyl)pentacarbonylrhenium (8) was prepared in an identical fashion from complex 6: IR (hexanes) identical with that of **7**; ^{1}H NMR ($CDCl_3$) δ 6.20 (s, C=CH), 1.20 (s, CMe_3); ^{13}C NMR identical with that of 6 except ReCD resonance obscured by those of *t*-Bu group; mass spectrum (using ^{187}Re), *m/e* 423 (P^+), 395 ($P^+ - CO$), 367 ($P^+ - 2CO$), 339 ($P^+ - 3CO$), 311 ($P^+ - 4CO$), 96 (C_3HD-*t*-Bu). Anal. C, H.

((2,3-Diphenyl-2-cyclopropen-1-yl)carbonyl)pentacarbonylmanganese (10) was prepared from $Na[Mn(CO)_5]$ (3.0 mmol) and 2,3-diphenyl-2-cyclopropene-1-carbonyl chloride (3.1 mmol) in a manner identical with that described for **2** above. Complex **10** was isolated as yellow crystals: 0.85 g, 68%; mp 89 °C; IR (hexanes) ν_{CO} 2112 (w), 2047 (w), 2007 (vs), 1995 (s), 1623 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.44 (s, C*H*), 7.10–7.80 (m, Ph); ^{13}C NMR ($CDCl_3$) δ 265.15 (C=O), 209 (br, C≡O), 130.10, 129.69, 128.96, 127.25 (Ph), 112.81 (C=*C*Ph), 50.07 (CH); mass spectrum, *m/e* 414 (P^+), 386 ($P^+ - CO$), 358 ($P^+ - 2CO$), 330 ($P^+ - 3CO$), 302 ($P^+ - 4CO$), 274 ($P^+ - 5CO$), 246 ($P^+ - 6CO$), 191 (C_3Ph_2H). Anal. C, H.

Decomposition of 10. A solution of **10** (0.50 g, 1.2 mmol) in Et_2O (20 mL) was stirred overnight at 20 °C and then evaporated to dryness. The residue was chromatographed on a 15 × 1 cm silica gel/hexanes column, eluting with hexanes, to yield first a pale yellow band which afforded $[Mn_2(CO)_{10}]$ (0.20 g, 85%), identified by its IR spectrum, and then a colorless eluate which afforded white crystalline 1,2,4,5-tetraphenylbenzene: 0.21 g, 96%; mass spectrum, *m/e* 382 (P^+); mp 263–265 °C (lit.[52] 265–266 °C).

(η-Cyclopentadienyl)((2,3-diphenyl-2-cyclopropen-1-yl)carbonyl)dicarbonyliron (11). A solution of $Na[Fe(\eta\text{-}C_5H_5)(CO)_2]$ (5.0 mmol) in THF (50 mL) was prepared by reducing $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ (2.5 mmol) with Na (10 mmol) in Hg (15 mL). The anion solution was filtered and cooled to −78 °C, and a solution of 2,3-diphenyl-2-cyclopropene-1-carbonyl chloride (5.0 mmol) in THF (10 mL) was added dropwise. The mixture was stirred for 1 h at −78 °C and warmed to ambient temperature, and the THF was removed under vacuum. The residue was extracted with CH_2Cl_2 (50 mL), filtered, evaporated to dryness, and chromatographed on a 15 × 2 cm florisil/hexanes column. Hexanes eluted traces of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$, and Et_2O eluted a yellow band, which was evaporated to dryness and recrystallized from CH_2Cl_2/hexanes (−30 °C) to give **11** as yellow crystals: 1.39 g, 70%;

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(53) This ordering stems from the expectation that a suprafacial [1,5]-sigmatropic shift is orbital symmetry allowed and that activation energies for forbidden suprafacial [1,7]- and [1,3]-sigmatropic shifts should show attentuation for the larger ring. Wilcox and Carpenter[54] have obtained good results in modeling the transition states of hydrocarbon pericyclic reactions using the π-isoconjugate ground-state structure. Thus a [1,5]-sigmatropic shift in cyclopentadiene involves a transition state which can be represented by the π orbitals of bicyclo[3.1.0]hexatriene, and its energy can be calculated in terms of its π energy E_π. The energy difference, ΔE_π, between the ground and transition states can then be obtained. The success of this approach lies in an *empirically* observed correlation between calculated $\Delta(\Delta E_\pi)$ and observed $\Delta(\Delta H^\ddagger)$ for a variety of pericyclic reactions. Application of the formula $\Delta(\Delta H^\ddagger) = 20.33\Delta(\Delta E_\pi) \pm 1.7$ kcal·mol^{-1} to our systems of interest results in the prediction that a [1,7]-sigmatropic shift should be ca. 7 kcal·mol^{-1} more favorable than the [1,3] shift. In turn a [1,5]-sigmatropic shift should be ca. 9 kcal·mol^{-1} more favorable than a [1,7] shift. Differences in strain energies between transition states are ignored, but these would probably accentuate the difference between [1,7] and [1,3]. It should be noted that the observation that $[Re(\eta^1\text{-}C_7H_7)(CO)_5]$[18] and $[Ru(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_7H_7)(CO)_2]$[55] undergo [1,7] shifts of the metal at lower energy than [1,5] shifts clearly run counter to this argument and serve to emphasize the general lack of understanding of the mechanisms of this type of dynamic behavior.

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mp 85–87 °C; IR (hexanes) ν_{CO} 2016 (s), 1960 (s), 1638 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 4.76 (s, C_5H_5), 3.45 (s, CH), 7.2–7.8 (m, Ph); ^{13}C NMR (CDCl$_3$) δ 262.8 (C=O), 214.7 (C≡O), 129.70, 128.96, 128.64, 127.91 (Ph), 112.41 (Ph*C*=C), 86.36 (C_5H_5), 47.56 (CH); mass spectrum, *m/e* 396 (P$^+$), 368 (P$^+$ – CO), 340 (P$^+$ – 2CO), 191 (C_3HPh_2). Anal. C, H.

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Registry No. 2, 79643-31-5; **3**, 79643-33-7; **5**, 79643-34-8; 6, 79647-57-7; **7**, 79643-32-6; **8**, 79643-24-6; **10**, 82495-39-4; **11**, 69302-82-5; [Re$_2$(CO)$_{10}$], 14285-68-8; [Re(CO)$_5$]$^-$, 14971-38-1; Na[Mn(CO)$_5$], 13859-41-1; Na[Fe(η-C_{H5})(CO)$_2$], 12152-20-4; [Fe$_2$(η-C_5H_5)$_2$(CO)$_4$], 12154-95-9; 2,3-diphenyl-2-cyclopropene-1-carbonyl chloride, 6415-58-3; 2-*tert*-butyl-2-cyclopropene-1-carbonyl chloride, 82495-40-7; 2-*tert*-butyl-3-deuterio-2-cyclopropene-1-carbonyl chloride, 82495-41-8.

Mechanism of Formation of (η^3-Oxocyclobutenyl)cobalt Compounds from [Co(CO)$_4$]$^-$ and Cyclopropenium Cations

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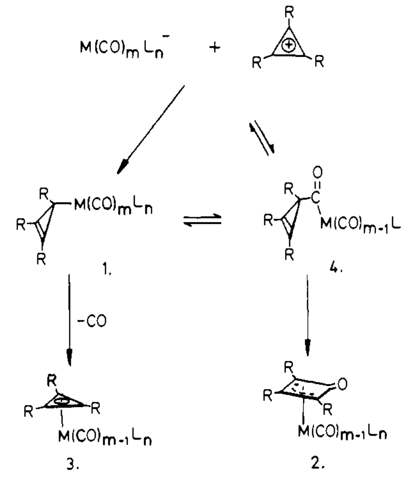
Abstract: 2-Cyclopropene-1-carbonyl chlorides **6** react with [Co(CO)$_4$]$^-$ in MeCN, THF, or C_6H_6 solution to afford (η^3-oxocyclobutenyl)tricarbonylcobalt complexes **7**. No η^3-cyclopropenyl compounds of cobalt are produced. The reaction is shown to proceed by initial formation of a coordinatively saturated (2-cyclopropen-1-ylcarbonyl)tetracarbonylcobalt species, which then undergoes decarbonylation to afford a coordinatively unsaturated (2-cyclopropen-1-ylcarbonyl)tricarbonylcobalt intermediate. ^{2}H and ^{13}C labeling studies confirm that this intermediate is the crucial precursor for ring expansion to the oxocyclobutenyl ligand. In THF or MeCN solution this intermediate is in dynamic equilibrium with a cyclopropenium cation and [Co(CO)$_4$]$^-$; in less polar C_6H_6 this equilibrium is insignificant. Evidence is presented that reactions of cyclopropenium cations with [Co(CO)$_4$]$^-$ involve direct electrophilic attack at a CO ligand rather than at cobalt; no evidence for the presence of η^1-cyclopropenyl cobalt intermediates has been obtained. In C_6H_6, chiral acyl chlorides **6** afford chiral oxocyclobutenyl compounds **7**; in THF or MeCN only racemic products are obtained due to the dissociative equilibrium mentioned above. The effects of ring substituents on the selectivity of C–C cleavage in the ring expansion step resemble those obtained in photochemical rather than thermal ring openings of cyclopropenes. A ring expansion mechanism which involves a metal-stabilized vinylcarbene transition state is proposed; this transition state collapses to a nonplanar vinylketene species which undergoes ring closure to the oxocyclobutenyl ligand. ^{1}H and ^{13}C NMR data for a large number of (oxocyclobutenyl)cobalt compounds are presented.

Introduction

Reactions of cyclopropenium cations with low-valent metal centers which lead to (η^3-cyclopropenyl)- and (η^1-cyclopropenyl)metal complexes have been surveyed in the preceding paper,[2] and a new synthesis of nonfluxional η^1-cyclopropenyl compounds of rhenium via the facile thermal decarbonylation of (2-cyclopropen-1-ylcarbonyl)pentacarbonyl rhenium complexes was described.[3] Curiously, reactions of cyclopropenium cations with metal carbonyl anions only rarely lead to formation of η^1-cyclopropenyl compounds **1**[4,5] but instead afford η^3-oxocyclobutenyl complexes **2**[6–9] in an intriguing reaction by which CO is incorporated into the three-membered ring.

Scheme I illustrates anticipated interconversions between η^1-cyclopropenyl compounds **1**, η^3-cyclopropenyl systems **3**, and η^3-oxocyclobutenyl complexes **2**; literature precedents for each step have been reported, though not all for the same system. The triphenylcyclopropenium cation has been shown to react with [Fe(η-C_5H_5)(CO)$_2$]$^-$ to afford the η^1-cyclopropenyl compound **1** (R = Ph; M = Fe(η-C_5H_5)(CO)$_2$),[4,5] whereas the tri-*tert*-butylcyclopropenium cation reacts with the same anion to afford only **2** (R = *t*-Bu; M = Fe(η-C_5H_5)(CO)).[10] It was proposed that the latter reaction, for steric reasons, proceeded via direct electrophilic attack at a CO ligand rather than at the metal, to give a coordinatively unsaturated 2-cyclopropene-1-carbonyl intermediate **4** (M = Fe(η-C_5H_5)(CO)) which then underwent ring

Scheme I



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