Selective reductions of carbonyl compounds with group 6 metal carbonyl hydrides

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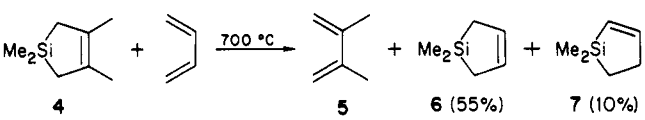
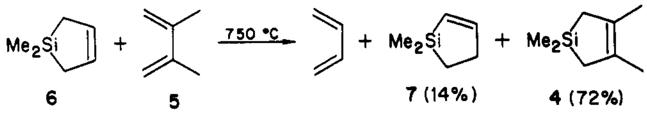
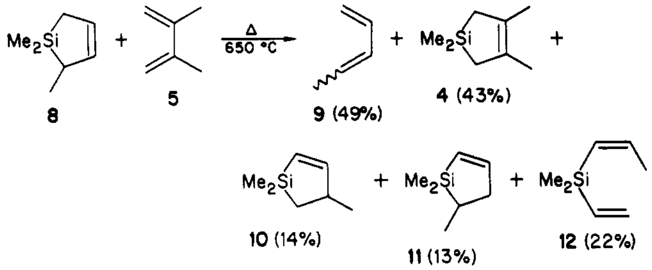


The formation of 1,1-dimethyl-1-silacyclopent-2-ene (**7**) in addition to the formal 1,4-adduct **6** is probably due to isomerization of **6** to **7** under the reaction conditions. When pure **6** is subjected to pyrolysis at 750 °C (1 torr), a 16% yield of **7** was obtained in addition to 53% butadiene (69% decomposition of **6**). In the presence of excess dimethylbutadiene **5** (**5**:**6** = 5), the expected product of dimethylsilylene-transfer was obtained, and the conversion of starting material (70% decomposition of **6**) was the same as in the absence of trapping agent.



From these results it appears that the loss of the Me$_2$Si unit from silacyclopent-3-enes **4** and **6** is reversible and unimolecular, and thus it is fair to conclude that extrusion of dimethylsilylene occurs. There is in addition clear evidence for nonconcerted extrusion[12] in the pyrolysis of 1,1,2-trimethyl-1-silacyclopent-3-ene (**8**), synthesized by the elegant method of Conlin,[13] in the presence of 2,3-dimethylbutadiene (**5**).



We see that in addition to the product of silylene transfer **4**, there is an equal yield of intramolecular rearrangement products **10**, **11**, and **12**. These latter products have also been obtained in the addition of Me$_2$Si: to the piperylenes **9**,[8] but in the present experiment the large excess of **5** over **9** ensures that the extruded silylene is captured by **5**. The formation of **10**, **11**, and **12** is most easily rationalized in terms of carbon–carbon bond cleavage in the alkenylsilirane intermediates **13**, **14**, and **15** shown in Scheme I.

Since products **10**, **11**, and **12** are formed, together with **8**, in the addition of Me$_2$Si to *cis*- and *trans*-piperylene **9**,[8,14] loss of dimethylsilylene from 1,1,2-trimethyl-1-silacyclopent-3-ene (**8**) appears to be the inverse of the silylene addition. It is therefore hardly surprising that the same alkenylsilirane intermediates **13**, **14**, and **15** are proposed for the extrusion pictured above as for the previously studied silylene addition. Once the addition has been shown to be reversible, the extrusion must follow the same mechanism.

We thus conclude that extrusion of dimethylsilylene from trimethylsilacyclopentene (**8**) is a nonconcerted process whose ultimate step is the loss of Me$_2$Si: from alkenylsilirane intermediates. The mechanism of dimethylsilylene extrusion from 1,1-dimethyl-1-silacyclopent-3-ene (**6**) and other related processes including the extrusion of dichlorosilylene from 1,1-dichloro-1-silacyclopent-3-enes[4] must be regarded as remaining an open question until tests for the concertedness are applied.

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Registry No. 4, 16109-39-0; 5, 513-81-5; 6, 16054-12-9; 7, 18187-50-3; 8, 3528-14-1; 9, 504-60-9; 10, 93297-71-3; 11, 93297-70-2; 12, 93297-72-4; butadiene, 106-99-0.

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[12] A small contribution from concerted extrusion is not precluded by these data.

[13] Conlin, R. T.; Peterson, L. L. *J. Organomet. Chem.* **1982**, *232*, C71.

[14] Differences in temperature account for *differences* between the product ratios reported here from the pyrolysis of the silacyclopentene and those reported in ref 8 for the addition of Me$_2$Si: to the piperylenes.

Selective Reductions of Carbonyl Compounds with Group 6 Metal Carbonyl Hydrides

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Summary: Aldehydes were selectively reduced to alcohols in the presence of ketones by Et$_4$N[μ-HMo$_2$(CO)$_{10}$] and HOAc in refluxing THF; α,β-unsaturated esters or ketones were reduced at the carbon–carbon double bond only. After prolonged reaction with excess reducing agent, an unhindered cyclohexanone was partially reduced with high stereoselectivity.

Since reductions of carbonyl groups represent one of the most fundamental transformations in organic chemistry, new reagents which can function as selective reducing agents are always being sought. Although a number of reagents will discriminate fairly well between an aldehyde and a methyl ketone, one of the most difficult tests for a chemoselective reducing agent is the discrimination between aldehydes and unhindered cyclohexanones. All of the reagents previously reported to demonstrate this type of selectivity are stoichiometric rather than catalytic agents and most are main-group hydride derivatives;[1] typically, the selectivity results from diminished activity and steric bulk. Although the reagents are effective in performing selective reductions, some shortcomings can be identified for each of them. In general, the adverse features are their relatively great expense (magnified by their stoichiometric nature) and/or their moisture sensitivity.

In contrast to main-group metal hydrides, transition-metal hydrides have been studied very little as reducing agents for organic compounds. The one most studied is the hydridotetracarbonylferrate, [HFe(CO)$_4$]$^-$, which is effective in reducing a variety of functional groups but is difficult to handle.[2] The related binuclear anion [HFe$_2$(CO)$_8$]$^-$, reduces carbon–carbon double bonds in activated compounds but does not reduce carbonyl groups.[3] Organic

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Table I. Reductions Utilizing $Et_4N[\mu\text{-}HMo_2(CO)_{10}]$[a]

substr	substr:μ-hydride:HOAc, mol	time, h	prod mixt, rel %[b]
PhCH=CHCHO	1:4:4	5	$PhCH_2CH_2CH_3$, 12 $PhCH_2CH_2CHO$, 3 $PhCH_2CH_2CH_2OH$, 85
PhCH=CHCOMe	1:4:4	5	$PhCH_2CH_2COMe$ 100[c]
PhCH=CHCOOEt	1:4:4	12	$PhCH_2CH_2COOEt$, 94 PhCH=CHCOOEt, 6
Me_2C=CHCOMe	1:4:4	15	Me_2CHCH_2COMe, 98 Me_2C=CHCOMe, 2
$PhCH_2CH_2CHO$	1:2:2	5	$PhCH_2CH_2CH_3$, 2 $PhCH_2CH_2CH_2OH$, 98
$PhCH_2CH_2CHO$	1:1:1	3	$PhCH_2CH_2CH_2OH$, 100
$PhCH_2CH_2CHO$ and 4-*tert*-butylcyclohexanone	1:1:1:1	3	$PhCH_2CH_2CH_2OH$, 50 4-*tert*-butylcyclohexanone, 50 4-*tert*-butylcyclohexanols, 0
4-*tert*-butylcyclohexanone	1:4:4	12	4-*tert*-butylcyclohexanone, 70[c] *cis*-4-butylcyclohexanol, 28 *trans*-4-*tert*-butylcyclohexanol, 2
$PhCH_2CH_2CHO$ and $PhCOCH_3$	0.5:0.5:2:2	3	$PhCH_2CH_2CH_2OH$, 50 PhCOMe, 50

[a] All reactions were conducted in refluxing THF. [b] Relative percentages were determined by GC. [c] Relative percentages were determined by ^1H NMR.

carbonyl groups are reduced by $[HM(CO)_5]^-$ (M = Cr, W),[4] but these, also, are highly moisture sensitive and difficult to handle.[5] We have begun to investigate the applications of group 6 binuclear hydrido anions $Et_4N[\mu\text{-}HM_2(CO)_{10}]$ (M = Mo and W) in combination with acetic acid; in this paper we describe their utility as selective reducing agents.

The results of our studies are summarized in the Table I. Simple methyl ketones show no evidence of reduction under conditions where aldehydes are reduced completely to alcohols. Methyl ketones or esters which are α,β-unsaturated were reduced at the double bond only. In a competitive experiment, 4-*tert*-butylcyclohexanone showed no evidence of reduction while hydrocinnamaldehyde was reduced to the alcohol completely. Thus, the reagent is comparable to the best of the selective reducing agents previously used to discriminate between an aldehyde and an unhindered cyclohexanone.[1a,d-f] Although Table I provides only relative percentages of compounds in the product mixture, isolated yields are quite high.[6]

In a prolonged experiment with excess reducing agent, 4-*tert*-butylcyclohexanone was reduced to the extent of about 30%; the reduction was highly stereoselective, providing the cis alcohol primarily (93%). Although the conversion of the ketone was low after 12 h, the selectivity of the reagent is comparable to lithium tri-*sec*-butylborohydride.[7]

Reductions of cinnamaldehyde or hydrocinnamaldehyde conducted with excess reducing agent yielded a small amount of *n*-propylbenzene. This type of product has not been observed in reductions of aldehydes by $[HM(CO)_5]^{-5a,b}$ nor is it a normal result in borohydride reductions. The results suggest that conversion of alcohols to hydrocarbons may be effected with these reagents; this point is being examined further.

Most reductions with $[\mu\text{-}HMo_2(CO)_{10}]^-$ can be completed within a few hours (see Table I). By comparison, reductions of cinnamaldehyde with $Et_4N[\mu\text{-}HW_2(CO)_{10}]$ and HOAc (1:4:4) require 8–9 days for completion and yield small amounts of cinnamyl alcohol in addition to the other products afforded by the molybdenum hydride; the saturated alcohol is the major product (88%) of these reductions also.

The molybdenum hydride is a stable compound and is not moisture-sensitive nor highly air-sensitive; it has a long shelf life and is easy to handle. It can be readily synthesized by ion-pair extraction from $Mo(CO)_6$ and KOH in the same manner we described earlier for the chromium and tungsten complexes[5c] or by reaction of the dianion[8] with water. The hydride was degraded to $Mo(CO)_6$ in the course of the reductions, and this could be recovered and recycled. At present, the number of moles of $Mo(CO)_6$ recovered approximately equals the number of moles of μ-hydride used; we have not yet tried to increase this further by doing the reactions in a CO atmosphere. Since $Mo(CO)_6$ is used and then partially recovered, the procedure is semicatalytic at present.

The mechanism of these reductions is not presently understood. IR spectral data taken while reductions were in progress show no evidence for the presence of $[HMo(CO)_5]^-$ in the mixtures; thus, it is not clear whether dissociation of the μ-hydride takes place or not. Work is in progress to establish the course of the reactions and the

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(6) (a) A preparative reduction of hydrocinnamaldehyde was accomplished as follows: 1.5 g (11 mmol) of hydrocinnamaldehyde was dissolved in THF together with 6.7 g (11 mmol) of $Et_4N[\mu\text{-}HMo_2(CO)_{10}]$ and 0.7 g (11 mmol) of HOAc. The mixture was heated to reflux and maintained under nitrogen at 65 °C for 3 h. The mixture was then cooled to room temperature, and solvent was removed on a rotary evaporator. The residue was extracted with three small portions of ether, and the combined extracts were chilled to −30 °C to induce crystallization of $Mo(CO)_6$. After filtration to remove $Mo(CO)_6$, the ether extracts were concentrated and chilled again to effect the further removal of $Mo(CO)_6$. Ether was then evaporated, and the residue was distilled under vacuum; the yield of pure 3-phenyl-1-propanol (identical with an authentic commercial sample) was 1.2 g (78%). (b) In a similar manner, 1.5 g of ethyl cinnamate was heated in refluxing THF together with 2 molar equiv each of the molybdenum μ-hydride and HOAc for 12 h. The mixture was worked up as described above, and the product was distilled under vacuum; the yield of pure ethyl hydrocinnamate was 1.2 g (80%). An excess of HOAc and the μ-hydride is necessary since some degradation of the μ-hydride occurs upon prolonged heating. (c) Benzalacetone (2.0 g) was reduced with equimolar quantities of the μ-hydride and HOAc as described in **6a**. The reaction required 5 h and afforded 1.6 g (78% yield) of pure 4-phenyl-2-butanone after vacuum distillation. (d) Mesityl oxide (1.5 g) was reduced with 2 molar equiv each of the μ-hydride and HOAc as described in **6b**. The mixture was concentrated by distillation of most of the THF and then chilled to effect precipitation of $Mo(CO)_6$ and other byproducts. The solution was then distilled to effect separation of the product from residual THF; 4-methyl-2-pentanone was isolated in 75% yield (1.14 g).

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limits of usefulness of such reagents for selective functional group transformations.

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Registry No. Et$_4$N[μ-HMo$_2$(CO)$_{10}$], 12082-98-3; Et$_4$N[μ-HW$_2$(CO)$_{10}$], 12083-01-1; PhCH=CHCHO, 104-55-2; PhCH=CHCH$_2$OH, 104-54-1; Mo(CO)$_6$, 13939-06-5; KOH, 1310-58-3; Ph(CH$_2$)$_3$OH, 122-97-4; PhCH=CHC(O)CH$_3$, 122-57-6; PhCH=CHC(O)OEt, 103-36-6; (CH$_3$)$_2$C=CHC(O)CH$_3$, 141-79-7; PhC(O)CH$_3$, 98-86-2; Ph(CH$_2$)$_2$C(O)CH$_3$, 2550-26-7; Ph(CH$_2$)$_2$C(O)OEt, 2021-28-5; (CH$_3$)$_2$CHCH$_2$C(O)CH$_3$, 108-10-1; Ph(CH$_2$)$_2$CH$_3$, 103-65-1; Ph(CH$_2$)$_2$CHO, 104-53-0; *cis*-4-*tert*-butylcyclohexanol, 937-05-3; 4-*tert*-butylcyclohexanone, 98-53-3; *trans*-4-*tert*-butylcyclohexanol, 21862-63-5.

Activation of the M–CO Bond in Transition-Metal Complexes. $Fe_2(CO)_6(SMe)_2$ and Phosphine-Substituted Derivatives as Good Catalysts in Metal Carbonyl Substitution Reactions

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Summary: The catalytic activity of $Fe_2(CO)_6(SMe)_2$ in CO substitution reactions on several transition-metal carbonyl complexes is reported and compared with the results obtained with other reagents. Experimental evidence has been gained to support the view that radical species are involved in these reactions and a possible pathway is proposed to explain the catalytic cycle.

Carbon monoxide replacement reactions on transition-metal carbonyl complexes often require prolonged thermal activation which may cause extensive decomposition of the samples and consequently low yields of the desired substituted products.

Several reagents able to promote substitution of CO have been reported.[1] For instance, the use of trimethylamine *N*-oxide (Me$_3$NO) is now a well established procedure which often allows the synthesis of derivatives not accessible by thermal routes.[2] The oxidative decarbonylation by Me$_3$NO leads to a coordinatively unsaturated intermediate which readily reacts with other ligand present in the solution. Another well-studied compound is sodium benzophenone ketyl (BPK) whose ability to transfer an electron to the metal carbonyl affords a radical anion which undergoes facile CO substitution.[3] More recently, Coville and co-workers reported that the dimer [(C$_5$H$_5$)Fe(CO)$_2$]$_2$ also is a versatile catalyst for general ligand activation of metal carbonyls.[4] Although the catalytic mechanism has not been completely defined, cleavage of the metal–metal bond is presumed to be a key step in the process.

These observations prompted us to test the catalytic activity of other complexes containing metal–metal bonds. A better understanding of the mechanism operating in these catalytic processes can provide more insight into the basic chemistry of polynuclear metal carbonyl complexes.

The title compound Fe$_2$(CO)$_6$(SMe)$_2$ was chosen for the following reasons: (i) the presence of two bridging SMe ligands prevents the irreversible fragmentation of the catalyst (this feature is actually one of the main limitations in the use of [(C$_5$H$_5$)Fe(CO)$_2$]$_2$, particularly at high temperatures); (ii) the potential ability of the chalcogen to change its coordination bonding mode in order to equilibrate the electronic density inside the transition state. The reactivity of the Fe–Fe bond as well as the flexibility around the S–S axis in this molecule has been demonstrated already in the photochemically induced insertion reactions of acetylenes[6] and tetrafluoroethylene.[7]

The catalytic activity of this complex, we have found, is usually greater than that reported for [CpFe(CO)$_2$]$_2$ under the same experimental conditions. Furthermore, the catalytic activity markedly increases on going to the substituted Fe$_2$(CO)$_{6-x}$(PPh$_3$)$_x$(SMe)$_2$ (x = 1 or 2) derivatives, and no PPh$_3$/P(OMe)$_3$ exchange was noted when these complexes were employed as catalysts in the reaction between Ru$_3$(CO)$_{12}$ and P(OMe)$_3$. It is noteworthy that the title compound is able to catalyze reactions such as CO substitution in Mo(CO)$_6$ under conditions where [CpFe(CO)$_2$]$_2$ was not effective.[4a] Furthermore, the reaction between [CpFe(CO)$_2$]$_2$ and P(OEt)$_3$ in the presence of Fe$_2$(CO)$_6$(SMe)$_2$ afforded the monosubstituted product in high yields (80%) while the uncatalyzed thermal reaction[5] (benzene at reflux for 13 h) occurs with extensive decomposition which drastically reduces the yield. Also in the P(OEt)$_3$ substitution reactions of Fe$_3$(CO)$_{12}$ the yields of Fe$_3$(CO)$_{12-x}$[P(OEt)$_3$]$_x$ (x = 1–3) complexes are high since the mild conditions employed in our experiments do not favor irreversible cluster breakdown as observed in the thermal route.

In all the reactions studied the catalyst can be recovered almost quantitatively at the end of the experiment.

The involvement of radical species, formed by cleavage of the iron–iron bond, is favored by two observations: (a) the substitution reactions are markedly quenched by the addition of galvinoxyl to the reaction mixture, and (b) the detection of an ESR signal when an excess of a radical trap (PBN = α-phenyl-*tert*-butylnitrone) is added to a hydrocarbon solution of the catalyst at +40 °C. The intensity of this signal increases when the temperature is raised; stronger ESR signals are eventually observed from solutions of the Ph$_3$-substituted products in the same experimental conditions.

A possible mechanism to explain the catalytic activity of the title compound is shown in Scheme I.

An important feature in this pathway is the stabilization of the intermediate via the change in the coordination mode of the SMe ligand: electron transfer allows the

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