complete in 24 h. Spectroscopic data are reported in ref 9.

$ReI(MeC\equiv CMe)_3$ (2a). In oven-dried glassware, a suspension of 16.0 g (0.0144 mol) of **3** and 4.0 mL (0.051 mol) of $MeC\equiv CMe$ in 100 mL of C_6H_6 was stirred for 3 days at 25 °C. After filtration, the solvent was removed using a rotary evaporator. The yellow-brown oil was chromatographed on silica gel using 1:9 ethyl acetate/hexanes (v/v), and a broad yellow band was collected. After solvent removal, crystallization of the yellow oil from pentane (5 mL) gave large colorless to pale green crystals, contaminated with yellow crystals of **1a**, which were removed by hand. The yield of **2a** was 0.82 g (15% based on $KReO_4$). The major product of this synthesis is **1a**; yields of **2a** are variable, and occasionally none is obtained, for as yet undetermined reasons. **1a** could also be removed by sublimation at 75 °C or by conversion to $Re(O)Me(MeC\equiv CMe)_2$ with excess $ZnMe_2$ and chromatography.[12] IR: 1753 w, 1354, 1169, 1068, 1046, 826 w, 796 w, 719 w, 638 cm^{-1}. ^1H NMR: δ 2.74 (q, 1 Hz), 2.47 (q, 1 Hz) $CH_3C\equiv CCH'_3$. $^{13}C\{^1H\}$ NMR: δ 168.25, 157.08 $MeC\equiv CMe$; 18.90, 16.58 $CH_3C\equiv CCH_3$. MS: 476, 422. Anal. Calcd for $C_{12}H_{18}ReI$: C, 30.32; H, 3.82. Found: C, 30.66; H, 3.79.

$ReI(EtC\equiv CEt)_3$ (2b). Following the procedure for **2a**, 16.0 g (0.0144 mol) of **3** and 9.0 mL (0.080 mol) of $EtC\equiv CEt$ in 100 mL of C_6H_6 gave 0.69 g of **2b** (11% based on $KReO_4$). IR: 1738 w, 1724 w, 1413, 1305, 1254, 1151, 1099, 1064, 1050, 945, 810 w, 692 w cm^{-1}. ^1H NMR: δ 3.45 (q, 7 Hz), 3.05 (q, 7 Hz) $MeCH_2C\equiv CCH'_2Me$; 1.04 (t, 7 Hz), 0.96 (t, 7 Hz) $CH_3CH_2C\equiv CCH_2CH'_3$. $^{13}C\{^1H\}$ NMR: δ 171.81, 162.79 $EtC\equiv CEt$; 27.80, 27.30 $MeCH_2C\equiv CCH_2Me$; 14.76, 13.78 $CH_3CH_2C\equiv CCH_2CH_3$. MS: 560, 478. Anal. Calcd for $C_{18}H_{30}ReI$: C, 38.64; H, 5.40. Found: C, 38.38; H, 5.33.

$Re(O)(I)_3(PPh_3)_2$ (3)[10] was prepared following the procedure for the bromide derivative:[11] $KReO_4$ (8.0 g, 27.6 mmol) was dissolved in 24 mL of 57% aqueous HI (Aldrich), and a suspension of 34.3 g of PPh_3 (Pressure, 0.13 mol) in 500 mL of acetic acid was added. After the solution was stirred for 24 h, the yellow product was isolated by filtration and was washed with diethyl ether (4 × 100 mL) to afford 37 g of impure **3**, identified by its IR spectrum.[10] This product is used without further purification.

$[Re(MeC\equiv CMe)_3py]SbF_6$ (4). A solution of $AgSbF_6$ (36 mg, 0.11 mmol) in dry CH_2Cl_2 (15 mL vacuum transferred from CaH_2) was added to a mixture of **2a** (44 mg, 0.09 mmol) and pyridine (8.5 μL, 0.11 mmol) and the reaction mixture stirred for 3 days. Filtration, removal of the solvent to 1 mL, and addition of cold hexane (0 °C) yielded 59 mg of **4** as a pale yellow powder (96%). IR (neat): 1608 (py), 1225, 1175, 1075, 1050, 905, 765 s, 710 s cm^{-1}. ^1H NMR (CD_2Cl_2): δ 9.18, 8.32, 7.97 (all m) C_5H_5N, ortho, meta, para respectively; 3.15 (s), 2.26 (s) $CH_3C\equiv CCH'_3$. ^{13}C NMR (CD_2Cl_2): δ 181.25 (s), 158.67 (s) $MeC\equiv CMe$; 155.09 (d, 175 Hz), 140.28 (d, 166 Hz), 128.00 (d, 176 Hz) C_5H_5N; 18.20 (q, 130 Hz), 10.98 (q, 130 Hz) $CH_3C\equiv CCH_3$. Anal. Calcd for $C_{12}H_{18}ReI$: C, 30.78; H, 3.50. Found: C, 31.10; H, 3.47.

$Re(Me)(MeC\equiv CMe)_3$ (5). MeLi (0.1 mL of a 1.6 M solution in Et_2O, Aldrich, 160 mmol) was added to 46 mg of **2a** (0.10 mmol) in 6 mL of C_6H_6 at −78 °C. The mixture was stirred at 25 °C for 2.5 h, and after TLC showed the presence of unreacted **2**, another 0.2 mL of MeLi was added to the solution and stirring continued for a day. The solvent was removed in vacuo and the residue dissolved in CH_2Cl_2. This solution was filtered through silica gel and on evaporation of the volatiles yielded 21 mg (60%) of **5**, an off-white solid, in almost analytically pure form. IR: 1730 w, 1265, 1165 s, 1050, 740, 633 cm^{-1}. ^1H NMR (−20 °C, CD_3CN): δ 3.04 (s), 2.30 (s) $CH_3C\equiv CCH'_3$; 2.20 (s) $ReCH_3$. $^{13}C\{^1H\}$ NMR: δ 177.78, 163.66 $MeC\equiv CMe$; 18.91, 12.25 $CH_3C\equiv CCH_3$; 2.52, $ReCH_3$. Anal. Calcd for $C_{13}H_{21}Re$: C, 42.95; H, 5.82. Found: C, 43.60; H, 5.86.

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Registry No. **1a**, 90623-35-1; **1b**, 98778-24-6; **2a**, 121192-24-3; **2b**, 121210-57-9; **3**, 107060-21-9; **4**, 121192-26-5; **5**, 121192-27-6; $KReO_4$, 10466-65-6; 2-butyne, 503-17-3; 3-hexyne, 928-49-4.

Reactions of Homo- and Heterobinuclear Cobalt Carbonyls with Metal Carbonyl Hydrides

István Kovács, Attila Sisak, Ferenc Ungváry, and Lászlő Markő*

Institute of Organic Chemistry, University of Veszprém, Veszprém, H-8201, Hungary

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$HMn(CO)_5$, $HMo(CO)_3Cp$, and $HFe(CO)_2Cp$ (Cp = cyclopentadienyl) were found to react with $Co_2(CO)_8$ forming $HCo(CO)_4$ and the corresponding mixed-metal carbonyl dimers. It was shown that $HMo(CO)_3Cp$ transferred the hydrogen atom to $Co_2(CO)_8$ and $CoMn(CO)_9$ in reversible processes. The substituted hydride $HMn(CO)_4P$-*n*-Bu_3 and $Co_2(CO)_8$ afforded $(CO)_4CoMn(CO)_4P$-*n*-Bu_3 which was characterized by elementary analysis and IR and mass spectroscopy. Its reaction with $HMo(CO)_3Cp$ gave $HMn(CO)_4P$-*n*-Bu_3 and $CoMo(CO)_7Cp$. The attack of the hydrides took place in mixed-metal complexes exclusively on the cobalt atom. A mechanism in which the hydrides oxidatively add to a coordinatively unsaturated Co center formed by CO loss is proposed.

Introduction

Hydrogen atom transfer from transition-metal carbonyl as well as HMR_3-type (M = Si, Ge, Sn; R = alkyl, aryl) metalloid hydrides to dinuclear carbonyl complexes became one of the most controversial reactions in metal carbonyl chemistry. A great number of reports appeared in recent years showing that such transformations could proceed either by UV irradiation[1] and room light[2] or under thermal conditions.[3-5] In many cases mechanistic investigations were also carried out. Although several different pathways were suggested, all agreed in assigning a role for metal carbonyl radicals as reactive intermediates. However, there are examples where the earlier mechanistic

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considerations cannot be applied.[6]

Dicobalt octacarbonyl occupies an exceptionally important position among the metal carbonyl dimers, since hydrogen atom transfer from $HSiEt_3$ and $HCo(CO)_4$ to the corresponding cobalt carbonyl radicals is a presumed key step in catalytic hydrosilylation,[3d] isomerization,[7] and hydroformylation[8] of olefins. In addition, its reactions with silanes, germanes, and stannanes are of great utility in the preparation of M–Co bonded complexes.[3a–c] Interestingly, very little experimental information is known regarding the primary products and the molecular mechanism of these reactions of $Co_2(CO)_8$, in particular when metal carbonyl hydrides act as starting reagents. In fact, the transfer of H atoms from metal carbonyl hydrides under ambient conditions to any metal carbonyl dimer in mixed-metal systems has not yet been studied at all. We have now found and report some new, spontaneous hydrogen-exchange processes taking place between a cobalt and an other metal carbonyl center. The results contribute to the knowledge on the reactivity of mixed-metal carbonyls.[9] Furthermore, the reported reactions could serve as models of transformations that probably play an important role in homogeneous catalytic reactions where mixed-metal carbonyls and their hydrides are active species.[10]

Results and Discussion

$HMn(CO)_5$ (**1**) was observed to react smoothly with $Co_2(CO)_8$ (**2**) in heptane in the temperature range between 0 and 40 °C under an atmospheric pressure of carbon monoxide. With the hydride in a stoichiometric (2:1) ratio relative to **2** (present in 0.02 M concentration), the reaction according to eq 1 was complete in 15 min at 40 °C. At

$$2\underset{\mathbf{1}}{HMn(CO)_5} + \underset{\mathbf{2}}{Co_2(CO)_8} \rightarrow 2\underset{\mathbf{3}}{CoMn(CO)_9} + H_2 \quad (1)$$

this point the IR spectrum of the orange solution showed bands characteristic for the heterobimetallic compound **3** along with traces of $Mn_2(CO)_{10}$. The same amount of $Mn_2(CO)_{10}$ (about 5% of the starting hydride) was formed under the applied conditions also in the samples containing only **1** due to the extreme air sensitivity of the hydride and was therefore not a product of reaction 1. After column chromatography and crystallization **3** was obtained in pure form.

Experiments using $HMo(CO)_3Cp$ (**4**) and $HFe(CO)_2Cp$ showed that **2** was reactive also toward these hydrides giving the corresponding heterobimetallic complexes $CoMo(CO)_7Cp$ (**5**) and $CoFe(CO)_6Cp$. Practically quantitative yields could be obtained as indicated by IR spectroscopy. Evidently, a new, simple method was found for the preparation of mixed-metal carbonyl complexes of cobalt which has advantages as compared to some of the preparative procedures reported earlier.[11]

At 25 °C reaction 1 was slow enough to recognize the intermediate formation of $HCo(CO)_4$ (**6**) by its characteristic IR absorption bands, extensively overlapped with those of **3**. In order to trap **6** in the form of stable acyl- or alkylcobalt tetracarbonyls, reactions were started at 35 °C in the presence of a large excess of 1-heptene, styrene, or ethyl acrylate. Under such conditions CO was absorbed and the IR spectra of the reaction mixtures clearly showed the presence of the corresponding acyl or alkyl complexes,[8e,12,13] proving the formation of **6** according to eq 2. If no trap was employed, all of **6** decomposed to **2** during the reaction due to the catalytic effect of **2**.[8a] Consequently reaction 1 involves two separate steps as expressed in eq 2 and 3. Formation of **6** was unambiguously established

$$\underset{\mathbf{1}}{HMn(CO)_5} + \underset{\mathbf{2}}{Co_2(CO)_8} \rightarrow \underset{\mathbf{6}}{HCo(CO)_4} + \underset{\mathbf{3}}{CoMn(CO)_9} \quad (2)$$

$$2\underset{\mathbf{6}}{HCo(CO)_4} \rightarrow \underset{\mathbf{2}}{Co_2(CO)_8} + H_2 \quad (3)$$

also in two additional cases (when **4** and $HFe(CO)_2Cp$ reacted with **2** according to eq 4 and 5) based on its own

$$\underset{\mathbf{4}}{HMo(CO)_3Cp} + \underset{\mathbf{2}}{Co_2(CO)_8} \rightarrow \underset{\mathbf{6}}{HCo(CO)_4} + \underset{\mathbf{5}}{CoMo(CO)_7Cp} \quad (4)$$

$$HFe(CO)_2Cp + \underset{\mathbf{2}}{Co_2(CO)_8} \rightarrow \underset{\mathbf{6}}{HCo(CO)_4} + CoFe(CO)_6Cp \quad (5)$$

IR absorption frequencies or on those characteristic for the complexes formed with ethyl acrylate. The only other products were the corresponding heterobimetallic complexes **5** and $CoFe(CO)_6Cp$.

Hydrogen Atom Transfer Involving Phosphine-Substituted Metal Carbonyl Species. When $HCo(CO)_3PBu_3$ was added to **2** at 9 °C, an immediate formation of **6** and $Co_2(CO)_7PBu_3$ was observed (eq 6; R = *n*-Bu).

$$HCo(CO)_3PR_3 + \underset{\mathbf{2}}{Co_2(CO)_8} \rightarrow \underset{\mathbf{6}}{HCo(CO)_4} + Co_2(CO)_7PR_3 \quad (6)$$

When PBu_3 was replaced by $P(O\text{-}n\text{-}Bu)_3$, a similar fast reaction was observed (eq 6; R = *n*-BuO). Since these results may be interpreted also by phosphine exchange between the substituted hydrides and **2**, we deemed it advisable to investigate a two-metal system.

The reaction of $HMn(CO)_4PBu_3$ (**7**) and **2** at 40 °C in hexane solution gave an orange product. The IR spectrum of this solution in the ν(CO) range showed the presence of a single metal carbonyl. When bromine was added to the hexane solution of the complex, a greenish precipitate formed immediately ($CoBr_2$) and the remaining yellow solution showed bands at 2084 (m), 2019 (m), 2002 (vs), and 1948 (s) cm^{-1} characteristic for $BrMn(CO)_4PBu_3$. This spectrum was identical with an authentic one registered when $BrMn(CO)_5$ was reacted with PBu_3. Additional

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[6] Reference 5 reported hydrogen atom abstraction by $Cr(CO)_3Cp$ radicals from $HSnBu_3$; however, taking into account that $D(H–Cr) < D(H–Sn)$ (251[6a] and 293[6b] kJ mol^{-1}, respectively), the difference of *D* values cannot be the driving force of the reactions as it was suggested earlier in a general mechanism.[1c] (a) Landrum, J. T.; Hoff, C. D. *J. Organomet. Chem.* **1985**, *282*, 215. (b) Jackson, R. *J. Organomet. Chem.* **1979**, *166*, 17.

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analytical data confirmed that $(CO)_4CoMn(CO)_4PBu_3$ (**8**) was the compound formed in the reaction between **2** and **7**. The transient formation of **6** according to eq 7 could

$$\underset{\mathbf{7}}{HMn(CO)_4PBu_3} + \underset{\mathbf{2}}{Co_2(CO)_8} \rightarrow \underset{\mathbf{6}}{HCo(CO)_4} + \underset{\mathbf{8}}{(CO)_4CoMn(CO)_4PBu_3} \quad (7)$$

be observed at 25 °C in the IR spectra in a way similar to that described in the reactions of **2** with **1**, **4**, and $HFe(CO)_2Cp$. This suggests that the substitution of one CO with PBu_3 in **1** did not affect the reaction mechanism.

Complex **8** is a new compound that cannot be obtained by direct substitution or metathetical synthesis.[11a] In general, mixed-metal cobalt complexes can be substituted only on the cobalt atom. Only few examples of substituted manganese–cobalt compounds containing the substituent on the manganese have been reported previously.[11e,14]

When **4** was added to a hexane solution of **8** at 40 °C, the formation of **7** and **5** could be observed (eq 8).

$$\underset{\mathbf{4}}{HMo(CO)_3Cp} + \underset{\mathbf{8}}{(CO)_4CoMn(CO)_4PBu_3} \rightarrow \underset{\mathbf{7}}{HMn(CO)_4PBu_3} + \underset{\mathbf{5}}{CoMo(CO)_7Cp} \quad (8)$$

Unfortunately, experiments with some other combinations of phosphine-substituted cobalt carbonyls and manganese carbonyl hydrides did not give unequivocal results because of parallel ligand exchange processes.[15]

Reversible Hydrogen Atom Transfer Reactions. When **6** was added to **3** at 25 °C, no change in the IR band intensities of **3** could be observed indicating that reaction 1 is not reversible under these conditions. However, **5** was found to react with **6** forming **4** and **2** as depicted in eq 9.

$$\underset{\mathbf{6}}{HCo(CO)_4} + \underset{\mathbf{5}}{CoMo(CO)_7Cp} \rightarrow \underset{\mathbf{4}}{HMo(CO)_3Cp} + \underset{\mathbf{2}}{Co_2(CO)_8} \quad (9)$$

The overall changes of concentrations of three components of this system during a typical experiment are presented in Figure 1. H_2, **2**, and **5** were the final products in this system due to the decomposition of **6**. Reaction 9 is evidently the reverse of (4) which means that the transfer of H from **4** to **2** is a reversible process:

$$\underset{\mathbf{4}}{HMo(CO)_3Cp} + \underset{\mathbf{2}}{Co_2(CO)_8} \rightleftharpoons \underset{\mathbf{5}}{CoMo(CO)_7Cp} + \underset{\mathbf{6}}{HCo(CO)_4} \quad (10)$$

Since **6** proved to be too unstable to investigate a system free of competing secondary decomposition reactions, a reaction mixture containing three different metals was used to verify the reversibility of H exchange more spectacularly. Accordingly, when **1** was added to a heptane solution of **5** at 40 °C, **3** and **4** formed (eq 11) at a fair rate

$$\underset{\mathbf{1}}{HMn(CO)_5} + \underset{\mathbf{5}}{CoMo(CO)_7Cp} \rightleftharpoons \underset{\mathbf{3}}{CoMn(CO)_9} + \underset{\mathbf{4}}{HMo(CO)_3Cp} \quad (11)$$

which could be followed by IR spectroscopy. Figure 2a shows the concentration changes of the two mixed-metal carbonyls during a typical experiment. $MnMo(CO)_8Cp$ did not appear in detectable amounts. Repeating the process in the reverse direction, **3** and **4** produced solely **1** and **5** (Figure 2b and eq 11).

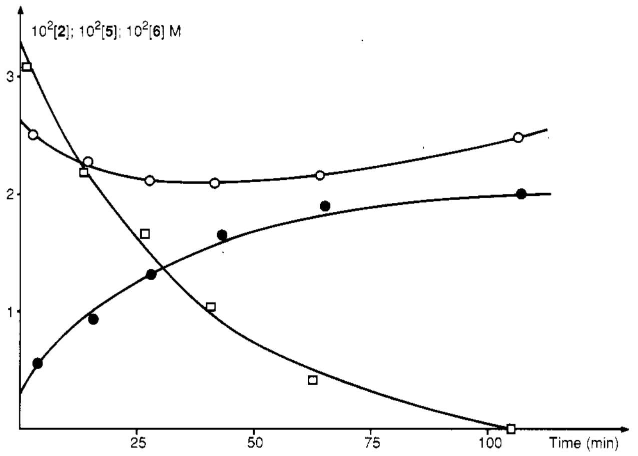

Figure 1. Concentration vs time plot for the decomposition of $HCo(CO)_4$ to $Co_2(CO)_8$ in the presence of $CoMo(CO)_7Cp$ at 25 °C in heptane under 1 atm of CO: (●) changes of [**2**]; (○) changes of [**5**]; (□) changes of [**6**]. The actual concentrations were determined by measuring the IR absorbances of **2** at 1857 cm^{-1} (ϵ_M = 1735 $cm^2\ mmol^{-1}$), **5** at 1978 cm^{-1} (ϵ_M = 7630 $cm^2\ mmol^{-1}$), and **6** at 2116 cm^{-1} (ϵ_M = 364 $cm^2\ mmol^{-1}$). The formation of **4** was also followed at 1940 cm^{-1}, but not measured quantitatively.

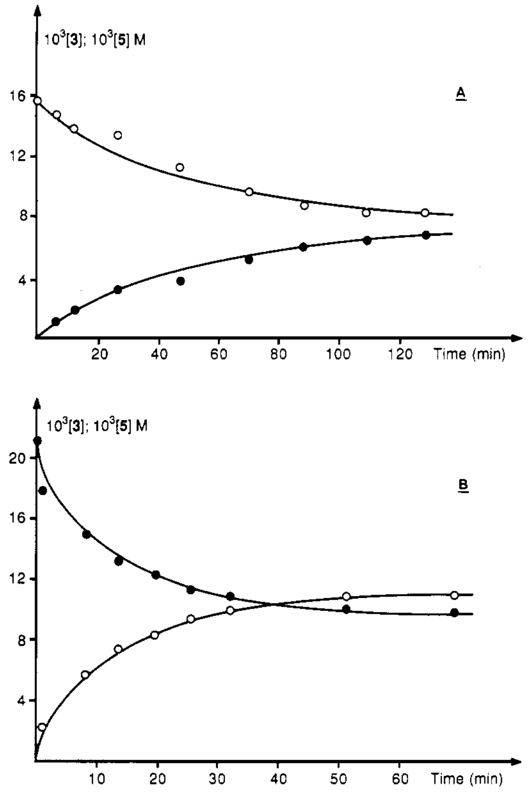

Figure 2. Concentration vs time plot for the reactions between (a) **4** and **3** and (b) **1** and **5** at 40 °C in hexane under 1 atm of CO: (○) changes of [**3**]; (●) changes of [**5**]. The actual concentrations were determined by measuring the IR absorbances of **3** at 2056 cm^{-1} (ϵ_M = 9870 $cm^2\ mmol^{-1}$) and **5** at 2075.5 cm^{-1} (ϵ_M = 4510 $cm^2\ mmol^{-1}$). The formation of **1** and **4** was established in the spectra at 2007 and 1940 cm^{-1}, respectively.

Our results provide the first experimental observation of reversible thermal hydrogen atom transfer in the case of transition-metal dimers as summarized in eq 10 and 11. The reversible oxidative addition of silanes to silylcobalt

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(15) Reactions of **2** with $HMn(CO)_3(PBu_3)_2$ and $HMn(CO)_3(dppe)$ and also those of $Co_2(CO)_7PPh_3$ and $Co_2(CO)_6(PBu_3)_2$ with **1** and **7** in various combinations were tested. A number of phosphine-substituted products formed, sometimes in secondary processes or at higher temperature (60–80 °C). Even $HMn(CO)_4PPh_3$ did not give the expected products with **2**, showing that the bulk and/or basicity of the ligand(s) has a remarkable influence on the reactivity of both the starting and product complexes. Additional work is needed to explore ligand effects on this reaction.

tetracarbonyls can be considered as the only precedent for such a process:[16]

$$R_3SiCo(CO)_4 + R'_3SiH \rightleftharpoons R'_3SiCo(CO)_4 + R_3SiH \quad (12)$$

As a conclusion, this work shows that reactions of metal carbonyl hydrides with homo- or heterobinuclear carbonyl complexes containing the $Co(CO)_4$ group lead to the formation of an other hydride in the first step. This process seems to be quite general.

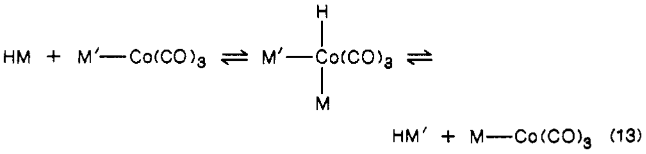
Mechanism. The formation of **6** is not in accordance with the mechanisms proposed for hydrogen atom transfer processes to metal carbonyl dimers resulting in the evolution of H_2 as the primary product. In all cases when UV-generated radicals abstracted the hydrogen atom from the starting hydride, the driving force was suggested to be the difference in H–M bond strengths. On the basis of published bond dissociation energy data, this possibility should be ruled out in the present case.[17] Our conclusion is supported by the observation[18] that among the possible metal carbonyl radicals $Co(CO)_4$ radicals are the least capable to abstract H atoms.

The phosphine-substituted derivatives of such radicals derived from either the starting hydride or dimer are expected to be labile and lose phosphine which can replace the carbonyl ligands in other metal carbonyl radicals present and thus give rise to a wide range of products.[2] In fact, when **7** acted as hydrogen source toward **2** or **4** reacted with **8**, only two products were observed in each case showing that PBu_3 remained localized on the manganese. Such a simple product distribution is hardly compatible with a radical mechanism, although the loss of PBu_3 from $Mn(CO)_4PBu_3$ may eventually be slow enough[19] to be neglected in comparison with the rate of radical recombination giving the product dimer **8**. Nevertheless the absence of recombination products (both homo- and heterobimetallic) in the above-mentioned three-metal systems, where the number of possible combinations is the highest, supports a nonradical pathway.

As a further argument against free-radical processes in our systems, it can be mentioned that under more drastic conditions heterobimetallic complexes (for example, **3**) readily rearrange in equilibrium reactions over metal carbonyl radicals to homobinuclear complexes.[11c] Since no such rearrangement was observed under our (much milder) conditions, the dissociation of metal–metal bonds cannot play an important role in the systems investigated.

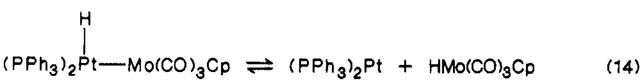
Experiments carried out under UV irradiation with heterobinuclear complexes[20] show that the dissociation of CO from one of the two metal centers takes place more easily than the cleavage of the metal–metal bonds. If there is a $Co(CO)_4$ group in the molecule, its relatively labile ligand sphere will act as the source of CO and therefore ligand substitution may take place on the cobalt probably without preliminary cleavage of the metal–metal bond.[11a,21] Accordingly, using an argon atmosphere instead of CO enhanced the formation of **5** (in eq 4), but the radical scavenger galvinoxyl had practically no influence on the rate.

Consequently the most probable mechanism for the reactions presented here involves fast dissociation of one CO ligand from the cobalt carbonyl moiety of the dimers. Oxidative addition of a hydride to the coordinatively unsaturated species formed in this way results in a hypothetical trinuclear intermediate. In the last step the same or the other hydride is reductively eliminated affording the known product distribution (eq 13). Our conclusion



$$HM + M'{-}Co(CO)_3 \rightleftharpoons M'{-}\underset{\textstyle M}{\overset{\textstyle H}{Co}}(CO)_3 \rightleftharpoons HM' + M{-}Co(CO)_3 \quad (13)$$

receives further support from a recent work[22] which explains the reversibility of the formation/decomposition of $(PPh_3)_2Pt(H)Mo(CO)_3Cp$ as oxidative addition/reductive elimination of **4** to (from) the coordinatively unsaturated $Pt(PPh_3)_2$ species (eq 14). Finally it is reasonable to



$$(PPh_3)_2\overset{\textstyle H}{Pt}{-}Mo(CO)_3Cp \rightleftharpoons (PPh_3)_2Pt + HMo(CO)_3Cp \quad (14)$$

suppose that hydrogen atom transfer takes place also in the homometallic system composed of **2** and **6** resulting in the exchange of cobalt atoms belonging to the two reactants.

Experimental Section

General Data. Infrared spectra were recorded on a Carl Zeiss Jena IR 75 spectrophotometer using 0.124- and 0.06-mm CaF_2 cuvettes. The GC–MS spectrum of **8** was recorded on a JMS 01-SG-2 JEOL spectrometer. All reactions were carried out under CO or Ar atmosphere in a thermostated glass reactor (±0.05 °C) wrapped in aluminum foil. The Schlenk technique was used for preparative purposes.

Materials. Heptane was distilled from sodium wire and benzophenone under CO or Ar. 1-Heptene, styrene, and ethyl acrylate were commercially available chemicals (EGA Chemie) redistilled and stored under CO. All of the hydrides and binuclear complexes were prepared by literature methods[23] and used mainly in stock solutions of heptane.

The purities and concentrations of hydrides in the stock solutions were determined by IR spectroscopy and quantitative metal analyses. If some decomposition occurred during storage and handling, the slightly soluble dimers of molybdenum and iron carbonyl crystallized on cooling and the concentration of the neat hydride solutions was corrected by repeated analyses. The traces

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(16) (a) Anderson, F. R.; Wrighton, M. S. *J. Am. Chem. Soc.* **1984**, *106*, 995. (b) Harrod, J. F.; Chalk, A. J. In *Organic Syntheses via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Wiley: New York, 1977; Vol. 2, pp 687–690.

(17) The order of relative H–M bond strengths in the metal carbonyl hydrides used in this work is the following: $HCo(CO)_4$ (230–239 kJ mol^{-1})[17a,b] < $HMn(CO)_5$ (225–272)[17a,c] < $HMo(CO)_3Cp$ (272).[6a] Several authors estimate that phosphine substituents could even strengthen these bonds;[1d,4] thus such hydrides are situated probably at the right-hand end of the above order. Evidently $HCo(CO)_4$ has the weakest H–M bond among the hydrides used. (a) Ziegler, T.; Tschinke, V.; Becke, A. *J. Am. Chem. Soc.* **1987**, *109*, 1351. (b) Ungváry, F. *J. Organomet. Chem.* **1972**, *36*, 363. (c) Connor, J. A.; Zafarani-Moattar, M. T.; Bickerton, J.; El-Saied, N. I.; Suradi, S.; Carson, R.; Altakhim, G.; Skinner, H. A. *Organometallics* **1982**, *1*, 1166.

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(20) (a) Sonnenberger, D.; Atwood, J. D. *J. Am. Chem. Soc.* **1980**, *102*, 3484. (b) Fletcher, S. C.; Poliakoff, M.; Turner, J. J. *J. Organomet. Chem.* **1984**, *268*, 259. (c) Johnston, P.; Hutchings, G. J.; Denner, L; Boeyens, J. C. A.; Coville, N. J. *Organometallics* **1987**, *6*, 1292. (d) Pope, K. R.; Wrighton, M. S. *Inorg. Chem.* **1987**, *26*, 2321.

(21) (a) Manning, A. R. *Inorg. Chim. Acta* **1979**, *33*, 45. (b) Manning, A. R. *J. Chem. Soc., Dalton Trans.* **1972**, 821. (c) Absi-Halabi, M.; Atwood, J. D.; Forbus, N. P.; Brown, T. L. *J. Am. Chem. Soc.* **1980**, *102*, 6248.

(22) Bars, O.; Braunstein, P.; Geoffroy, G. L.; Metz, B. *Organometallics* **1986**, *5*, 2021.

(23) References for the preparation of compounds $CoMo(CO)_7Cp$,[11f] $HMn(CO)_5$,[11d] $HCo(CO)_4$,[11d] and $HMn(CO)_4PBu_3$.[24a] $HMo(CO)_3Cp$ and $HFe(CO)_2Cp$ were obtained by the acidification of the anions[24b] with glacial acetic acid and subsequent workup as reported for $HMn(CO)_5$. $HCo(CO)_3PBu_3$ was prepared in situ from a heptane solution of $HCo(CO)_4$ by direct substitution with PBu_3. Its IR data were identical with those of the authentic compound.[24c]

(24) (a) Booth, B. L.; Haszeldine, R. N. *J. Chem. Soc. A* **1966**, 157. (b) Hayter, R. G. *Inorg. Chem.* **1963**, *2*, 1031. (c) Piacenti, F.; Bianchi, M.; Benedetti, E. *Chim. Ind. (Milan)* **1967**, *49*, 245.

of $Mn_2(CO)_{10}$ could not be separated from 1 by crystallization; thus the concentration of 1 was corrected with that of $Mn_2(CO)_{10}$ determined by IR. $Mn_2(CO)_{10}$ was indifferent in the studied reactions of 1.

In order to prepare 3 the published procedure[11a] was modified because the reaction between $NaCo(CO)_4$ and $BrMn(CO)_5$ was not complete in THF. To get satisfactory results, a 50-mL THF solution of 13 mmol of $NaCo(CO)_4$ and 10 mmol of $BrMn(CO)_5$ was evaporated in vacuo. This reaction took place only when the mixture was nearly dry. Then the residue was extracted with 5 × 10 mL portions of pentane, and 3 was crystallized at −78 °C. The product was obtained after column chromatography on silica in moderate yield (1.0 g, 2.7 mmol, 27%).

Preparation of $CoMn(CO)_9$ (3). A 0.8-mL aliquot of 0.187 M stock solution of 1 was added by a gastight Hamilton syringe to a solution of 2 (25 mg, 0.075 mmol) in 4.2 mL of heptane under an atmospheric pressure of CO. The formation of 3 was complete in 30 min at 40 °C, and the composition of this solution remained unchanged for an additional hour at room temperature as shown by IR. The solution was concentrated in vacuo and chromatographed on a 50 × 1 cm column packed with activated silica (0.2–0.5 mm, hexane eluant) to separate traces of $Mn_2(CO)_{10}$. The effluent was evaporated to dryness to give 37 mg (70% yield) of the red-orange mixed-metal complex 3. The IR spectrum of this product was identical with that of an authentic sample.[11a]

Preparation of $CoMo(CO)_7Cp$ (5). A 1.4-mL aliquot of a 0.143 M stock solution of 4 was syringed into 2 (34 mg, 0.1 mmol) dissolved in 3.6 mL of heptane at 30 °C under 1 atm of CO. The IR spectra showed complete disappearance of both 2 and 4 along with the formation of 5[11f] in 30 min. The solution was concentrated to 2 mL. Crystallization at dry ice temperature afforded 66 mg (80% yield) of red crystals of 5.

Preparation of $CoFe(CO)_6Cp$. A 2-mL aliquot of a 0.05 M solution of $HFe(CO)_2Cp$ in heptane was injected to a 3-mL heptane solution of 2 (17 mg, 0.05 mmol). The mixture was stirred at 30 °C under 1 atm of CO. The reaction was complete in 30 min when the IR spectrum of the solution showed only the bands of $CoFe(CO)_6Cp$.[11g] Concentration and crystallization at −78 °C gave 24 mg (70% yield) of red crystals of the title compound.

IR Observation of $HCo(CO)_4$ (6). Heptane solutions (5 mL) containing 2 (in 0.01 M concentration) and 1, 4, 7, $HFe(CO)_2Cp$, or $HCo(CO)_3PR_3$ (each in 0.02 M concentration) were stirred under 1 atm of CO at 9–25 °C. Samples were taken for analyses 5 min after the reactants were mixed. All three bands of 6 (2116 (w), 2052 (s), 2029 (vs) cm^{-1}) appeared separately and could be identified in the IR spectra except the case when 1 was used as the starting hydride. Three bands of 3 (2116.5 (w), 2056.2 (s), 2025.8 (vs) cm^{-1})[11a] extensively overlapped with those of 6, and only the peak at 2052 cm^{-1} could be identified clearly as a shoulder.

Reaction of 1 with 2 in the Presence of Olefins. The stock solution (0.9 mL) of 1 (39 mg, 0.2 mmol) was added under CO to the mixture of 2 (102 mg, 0.3 mmol) and 1.0 mmol of either 1-heptene, styrene, or ethyl acrylate in 4.1 mL of heptane at 35 °C. Gas uptake started immediately and its rate was measured in the first 5 min of the reaction. The total amounts of CO absorbed in 20 min were 8.8×10^{-2}, 6.0×10^{-2}, and 11.4×10^{-2} mmol, respectively. IR spectra were recorded after 30 min and showed intensive ν(CO) absorbances characteristic for $CH_3(CH_2)_6C(O)Co(CO)_4$,[12] $C_6H_5CH(CH_3)C(O)Co(CO)_4$,[13] and $C_2H_5OC(O)CH(CH_3)Co(CO)_4$ as well as $C_2H_5OC(O)(CH_2)_2C(O)Co(CO)_4$.[8e]

The Influence of Argon Atmosphere and Galvinoxyl on the Reaction between 2 and 4. On the basis of the increase of the IR band of 5 at 1978 cm^{-1} ($\epsilon_M = 7630$ cm^2 $mmol^{-1}$) during the reaction of 4 (25 mg, 0.1 mmol) with 2 (34 mg, 0.1 mmol) carried out in 5 mL of heptane at 15 °C, a 100% conversion of 4 into 5 was observed under 1 atm of argon atmosphere in 8 min in contrast to 40% achieved under CO. Repeating the experiment in the presence of 13 mg (0.03 mmol) of galvinoxyl, no significant change of the conversion (45%) was found under CO.

Preparation of $CoMn(CO)_8PBu_3$ (8). To a solution of 1 (227 mg, 1.16 mmol) in 3 mL of hexane was injected an equal amount of PBu_3 (288 μL, 1.16 mmol). After substitution was complete, the solution was transferred to an other Schlenk tube containing 2 (198 mg, 0.58 mmol). The mixture was left standing for 1 day at room temperature. IR analysis of a diluted sample showed the complete disappearance of the starting materials. The solvent was evaporated, and the remaining red oil was chromatographed on silica with hexane as eluent. Attempts to obtain crystals at −78 °C failed. Finally, 8 could be prepared in pure form as red oil in 60% yield (0.35 g). The material was stable in air during the sample preparation procedures for analyses. IR (in hexane): 2079 (m), 2030 (vs), 2002 (s), 1991 (s), 1982 (s, sh), 1947 (m) cm^{-1} in the C–O stretching region. Anal. Calcd for $C_{20}H_{27}O_8PCoMn$: C, 44.46; H, 5.04; Co, 10.91; Mn, 10.17. Found: C, 42.79; H, 5.47; Co, 10.05; Mn, 9.74. MS: *m/e* (assignment) 540 (M^+), 512 ($M^+ - CO$), 484 ($M^+ - 2CO$), 428 ($M^+ - 4CO$), 400 ($M^+ - 5CO$), 369 ($M^+ - 4CO - Co$), 341 ($M^+ - 5CO - Co$), 313 ($M^+ - 6CO - Co$), 285 ($M^+ - 7CO - Co$), 257 ($M^+ - 8CO - Co$).

Registry No. 1, 16972-33-1; 2, 10210-68-1; 3, 35646-82-3; 4, 12176-06-6; 5, 62015-65-0; 6, 16842-03-8; 7, 56960-19-1; 8, 121253-48-3; $CoFe(CO)_6Cp$, 34778-24-0; $HFe(CO)_2Cp$, 35913-82-7; $CH_3(CH_2)_6C(O)Co(CO)_4$, 121253-49-4; $C_6H_5CH(CH_3)C(O)Co(CO)_4$, 82182-04-5; $C_2H_5OC(O)CH(CH_3)Co(CO)_4$, 85421-34-7; $C_2H_5OC(O)(CH_2)_2C(O)Co(CO)_4$, 104465-50-1; 1-heptene, 592-76-7; styrene, 100-42-5; ethyl acrylate, 140-88-5.