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

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Registry No. $Et_4N[\mu-HMo_2(CO)_{10}]$, 12082-98-3; $Et_4N[\mu-$ HW₂(CO)₁₀], 12083-01-1; PhCH=CHCHO, 104-55-2; PhCH= CHCH₂OH, 104-54-1; Mo(CO)₆, 13939-06-5; KOH, 1310-58-3; Ph(CH₂)₃OH, 122-97-4; PhCH=CHC(O)CH₃, 122-57-6; PhCH= CHC(O)OEt, 103-36-6; (CH₃)₂C=CHC(O)CH₃, 141-79-7; PhC-(O)CH₃, 98-86-2; Ph(CH₂)₂C(O)CH₃, 2550-26-7; Ph(CH₂)₂C(O)OEt, 2021-28-5; (CH₃)₂CHCH₂C(O)CH₃, 108-10-1; Ph(CH₂)₂CH₃, 103-65-1; Ph(CH₂)₂CHO, 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. $Fe_2(CO)_8(SMe)_2$ and **Phosphine-Substituted Derivatives as Good Catalysts** in Metal Carbonyl Substitution Reactions

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Summary: The catalytic activity of Fe₂(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 transitionmetal 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 (Me₃NO) is now a well established procedure which often allows the synthesis of derivatives not accessible by thermal routes.² The oxidative decarbonylation by Me₃NO 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 $[(C_5H_5)Fe(CO)_2]_2$ 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 $[(C_5H_5)Fe(CO)_2]_2$, 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 acetylenes⁶ 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 reaction⁵ (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 $(PBN = \alpha$ -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 Ph₃-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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 Table I. Experimental Data for the Reaction between Metal Carbonyl Complexes and Lewis Bases in the Presence of Iron

 Dimers as Catalyst^a

				$[Fe(CO)_2(PPh_3)-SMe]_2$			$[(\eta^{5}-C_{5}H_{5})Fe-(CO)_{2}]_{2}$			thermal route		
_		molar		time,	Τ,	%	time,	Τ,	%	time,	Τ,	%
cluster	ligand	ratio	product	h	°C	yield	h	°C	yield	h	۳C	yield
$(\eta^5 - C_5 H_5) Fe(CO)_2 I$	PPh ₃	1:1	$(\eta^5 - C_5 H_5) Fe(CO)(PPh_3) I$	0.5	111	80	1.75	111	65^{b}	18	80	33.7^{e}
$(\eta^5 \cdot C_5 H_5) Fe(CO)_2 I$	PPh_3	1:1	$(\eta^5 - C_5 H_5) Fe(CO)(PPh_3) I$	3	80	90						
$(\eta^5 \cdot C_5 H_5) Fe(CO)_2 I$	CNCH ₂ Ph	1:1	$(\eta^5 - C_5 H_5) Fe(CO)(CNCH_2 Ph)I$	0.75	45	70	0.75	45	90^{b}	3	162	89/
$Mn_2(CO)_{10}$	PPh ₃	1:2	$Mn_2(CO)_8(PPh_3)_2$	0.75	111	90	1.5	111	80°	7	111	90 ^e
Mo(CO) ₆	PPh_3	1:2	$Mo(CO)_4(PPh_3)_2$	3	80	90	no	cat.	Ь		150 - 185	h
$[(\eta^{5}-C_{5}H_{5})Fe(CO)_{2}]_{2}$	$P(OEt)_3$	1:1.5	$(\eta^{5}-C_{5}H_{5})_{2}Fe_{2}(CO)_{3}P(OEt)_{3}$	3	80	85				13	80	i
Fe(CO) ₅	PPh ₃	1:1	$Fe(CO)_4PPh_3$	3	80	80	5	111	90°	3	110	3.5'
$Fe_3(CO)_{12}$	$P(OEt)_3$	1:1	$[Fe_{3}(CO)_{11}[P(OEt)_{3}]]$	15	25	80	15	25	60^d	3–6	50	17^{k}
$Fe_3(CO)_{12}$	$P(OEt)_3$	1:2	$[Fe_{3}(CO)_{10}[P(OEt)_{3}]_{2}]$	15	25	90	15	25	70^d	3-6	50	25^{k}
$Fe_3(CO)_{12}$	P(OEt) ₃	1:3	$[Fe_3(CO)_9[P(OEt)_3]_3]$	3.5	40	75	3.5	40	40^d	3–6	50	12*
$\operatorname{Ru}_3(\operatorname{CO})_{12}$	$P(OMe)_3$	1:3	$[Ru_3(CO)_9[P(OMe)_3]_3]$	1.5	45	85	3	45	85 ^d	1 - 3	67	7^l

^a All the reactions were carried out in cyclohexane, except those ones brought about at 111 °C which required toluene at the reflux, under N₂ flux, at the daylight. The reagent/catalyst molar ratio was 10:1. Typical runs involved 300 mg of carbonyl substrate dissolved in 150 mL of the appropriate solvent. All the compounds have been characterized by IR and ¹H and ³¹P NMR spectra. ^bReference 4a. ^cReference 4b. ^d This work. ^eTreichel, P. M.; Shubkin, R. L.; Barnett, K. W. and Reichard, D. *Inorg. Chem.* **1966**, 5, 1178. ^fJoshi, K. K.; Pauson, P. L.; Stubbs, W. H. J. Organomet. Chem. **1963**, 1, 51. ^gOsborn, A. G.; Stiddard, M. B. H. J. Chem. Soc. **1964**, 634. ^hDobson, G. R.; Stolz, I. W.; Sheline, R. K. Adv. Inorg. Chem. **1966**, 8, 1. ⁱ Haines, R. J.; Du Preez, A. L. Inorg. Chem. **1969**, 8, 1459. ^jCotton, F. A.; Parish, R. V. J. Chem. Soc. **1960**, 1440. ^kGrant, S. M.; Manning, A. R. Inorg. Chim. Acta **1978**, 31, 41. ^lBruce, M. I.; Shaw, G.; Stone, F. G. A. J. Chem. Soc. Dalton Trans. **1972**, 2094.



formation of a 17-electron metal center which is wellknown to undergo facile ligand substitution⁸ by an associative $S_N 2$ mechanism. The increased activity observed for the PPh₃-substituted derivatives can be accounted in terms of the steric hindrance of the bulky PPh₃ ligand which favors the flattening of the Fe₂S₂ tetrahedron with consequent weakening of the "bent" Fe–Fe bond. Finally, further insight into the operating mechanism has been gained by recording the ¹³C NMR spectrum of the solution in which the reaction between Ru₃(CO)₁₂ (~40% ¹³CO enriched) and P(OMe)₃ is taking place. As the reaction progresses, ¹³CO displacement can be easily followed whereas almost no 13 CO incorporation into the catalyst is detected.

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Registry No. $(\eta^{5}-C_{5}H_{5})Fe(CO)(PPh_{3})I, 12099-18-2; (\eta^{5}-C_{5}H_{5})Fe(CO)(CNCH_{2}Ph)I, 51567-84-1; Mn_{2}(CO)_{8}(PPh_{3})_{2}, 15279-67-1; Mo(CO)_{4}(PPh_{3})_{2}, 15096-70-5; (\eta^{5}-C_{5}H_{5})_{2}Fe_{2}(CO)_{3}P-(OEt)_{3}, 33057-34-0; Fe(CO)_{4}PPh_{3}, 35679-07-3; [Fe_{3}(CO)_{11}]P-(OEt)_{3}]], 69092-12-2; [Fe_{3}(CO)_{10}]P(OEt)_{3}]_{2}, 69092-23-5; (\eta^{5}-C_{5}H_{5})Fe(CO)_{2}], 12078-28-3; Mn_{2}(CO)_{10}, 10170-69-1; Mo(CO)_{6}, 13939-06-5; [(\eta^{5}-C_{5}H_{5})Fe(CO)_{2}]_{2}, 12154-95-9; Fe(CO)_{5}, 13463-40-6; Fe_{3}(CO)_{12}, 17685-52-8; Ru_{3}(CO)_{12}, 15243-33-1; PPh_{3}, 603-35-0; CNCH_{2}Ph, 10340-91-7; P(OEt)_{3}, 122-52-1; P(OMe)_{3}, 121-45-9; [Ru_{3}(CO)_{6}[P(OMe)_{3}]_{3}], 38686-18-9; [Fe(CO)_{2}(PPh_{3})SMe]_{2}, 63162-59-4; Fe_{2}(CO)_{6}(SMe)_{2}, 14878-96-7; [Fe_{3}(CO)_{9}[P(OMe)_{3}]_{3}], 96095-77-1.$

Preparation, Structure, and Reactivity of an Anionic Ruthenium Ketenyildene: $[PPN]_{2}[Ru_{3}(CO)_{6}(\mu-CO)_{3}(\mu_{3}-CCO)]$

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Summary: The new ketenylidene $[Ru_3(CO)_9CCO]^{2-}$ was prepared and fully characterized. The reaction with $CH_3OSO_2CF_3$ and H⁺ leads to attack at the CCO and the metal framework, respectively. Reaction with $Fe_2(CO)_9$ yields $[FeRu_3(CO)_{12}(C)]^{2-}$.

Recent discoveries have revealed the diverse chemistry of metal cluster ketenylidenes and related compounds with respect to C–O activation, cluster building, and carbon– carbon bond formation.¹⁻³ The origin of this varied

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