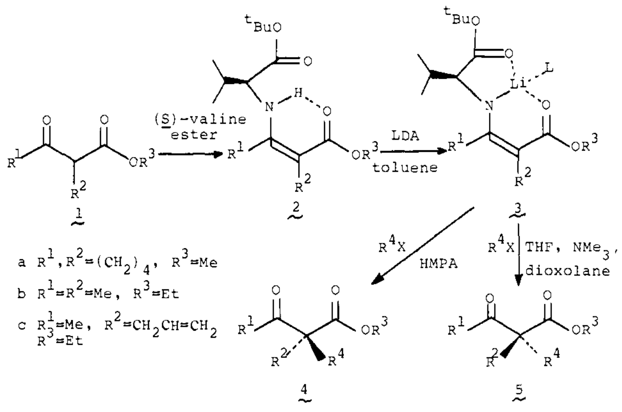
Table I. Asymmetric Alkylation of 2 Leading to 4 or 5 (Scheme I)[a]

entry	enamine[b]	R^4X (equiv)	ligand[c] (equiv)	4/5	isolated yield, %	$[\alpha]_D$,[d] deg	ee, %[e] (confn)
1	2a	MeI (1.2)	HMPT (1.0)	4a	57	−108	≥99 (R^f)
2	2a	MeI (5.0)	THF (2.0)	5a	63	−100	92 (S^f)
3	2a	$CH_2{=}CHCH_2Br$ (1.3)	HMPT (1.0)	4a	71	−102	76 (S^g)
4	2a	$CH_2{=}CHCH_2Br$ (5.0)	dioxolane (1.2)	5a	56	+75.2	56 (R^g)
5	2a	$PhCH_2Br$ (2.0)	HMPT (1.0)	4a	77	−111	≥99 (S^h)
6	2a	$PhCH_2Br$ (5.0)	dioxolane (1.6)	5a	48	+77.0	71 (R^h)
7	2a	$BrCH_2CO_2Me$ (2.0)	HMPT (1.0)	4a	59	−64.9	70 (S^h)
8	2a	$BrCH_2CO_2Me$ (2.0)	TMA (3.0)	5a	78	+69.2	74 (R^h)
9	2b	$CH_2{=}CHCH_2Br$ (2.0)	HMPT (1.0)	4b	68	−27.9	94 (S^i)
10	2b	$CH_2{=}CHCH_2Br$ (2.0)	dioxolane (2.0)	5b	20	+14.0	47 (R^i)
11	2b	$PhCH_2Br$ (2.0)	HMPT (1.0)	4b	90	−58.2	92 (S^j)
12	2b	$PhCH_2Br$ (5.0)	dioxolane (2.0)	5b	83	−57.0	90 (R^j)
13	2b	$BrCH_2CO_2Me$ (2.0)	HMPT (1.0)	4b	81	−30.6	76 (S^j)
14	2b	$BrCH_2CO_2Me$ (2.0)	TMA (3.0)	5b	76	+17.7	44 (R^j)
15	2c	MeI (2.0)	HMPT (1.0)	4c	54	+28.2	95 (R^i)
16	2c	MeI (2.0)	THF (1.6)	5c	66	−23.2	78 (S^i)

[a] For the reaction procedures, see the text. Reaction temperature: −55 °C (entries 1 and 3), −78 °C (entries 2, 4–16). [b] 2a, $[\alpha]^{25}_D$ +139° (benzene); 2b, $[\alpha]^{25}_D$ +153° (benzene); 2c, $[\alpha]^{25}_D$ +132° (benzene). [c] HMPT, hexamethylphosphoric triamide; THF, tetrahydrofuran; TMA, trimethylamine. [d] Optical rotations were taken in ethanol at 25 °C for entries 1–8 and in chloroform at 22 °C for entries 9–16. [e] These values were determined by the LIS-NMR technique ($Eu(hfc)_3$). [f] Absolute configuration was determined by correlating 4a (R^4 = Me) with (+)-(1*R*,2*R*)-(2-methyl-2-carboxycyclohexyl)acetic acid. Bachman, W. E.; Kushner, S. *J. Am. Chem. Soc.* 1943, *65*, 1963. Gautschi, F.; Jeger, O.; Prelog, V.; Woodward, R. B. *Helv. Chim. Acta* 1955, *38*, 296. [g] Absolute configuration was determined by correlation with the corresponding ethyl ester (NaOEt in ethanol). Frater, G. *Helv. Chim. Acta* 1980, *63*, 1383. [h] Absolute configuration was determined by correlating 4a ($R^4 = CH_2CH{=}CH_2$) and 4a ($R^4 = CH_2Ph$) with 4a ($R^4 = CH_2CO_2Me$) (ozonolysis, then methylation with diazomethane). [i] Frater, G. *Helv. Chim. Acta* 1979, *62*, 2825. [j] Absolute configuration was determined by correlating 4b ($R^4 = CH_2CH{=}CH_2$) and 4b ($R^4 = CH_2Ph$) with 4b ($R^4 = CH_2CO_2Me$) (ozonolysis, then methylation with diazomethane).

Scheme I



by the LIS-NMR technique ($Eu(hfc)_3$).

A number of general trends are evident from the data in the table. First, an opposite sense of asymmetric induction is found in the solvent system of toluene–HMPT on the one hand and systems toluene–THF, –dioxolane, or –trimethylamine on the other, with the former system exhibiting a somewhat greater selectivity. For example, in the reaction of **3a** with methyl iodide (entries 1 and 2), the enantiomeric excess was found to be over 99% in favor of **4a** (R^4 = Me) for the toluene–HMPT system and 92% in favor of **5a** (R^4 = Me) for the toluene–THF system. Second, in the synthesis of **5**, the appropriate combination of alkylating agent and ligand is of great importance in realizing a high level of asymmetric induction. For example, utilization of THF, dioxolane, and trimethylamine as the ligands in the methylation of **3a** with methyl iodide led to **5a** (R^4 = Me) (92% ee), **5a** (R^4 = Me) (64% ee), and **4a** (R^4 = Me) (3% ee), respectively. The appropriate combinations were found to be THF for methyl iodide, dioxolane for allyl bromide and benzyl bromide, and trimethylamine for methyl bromoacetate, but the reason for this is not yet clear. Third, asymmetric alkylation to each enantiomer can be realized regardless of whether cyclic or acylic β-keto esters are involved.[10]

In general, alkylation in toluene in the presence of HMPT as the ligand takes place preferentially from the top face of **3** to yield **4**, while in the presence of THF, dioxolane, or trimethylamine as the ligand it takes place from the bottom face of **3** to yield **5**. Further studies are in progress to elucidate this behavior.

Acknowledgment. Partial financial support from the Ministry of Education, Science and Culture, Japan (Grant-in-aid for Scientific Research, No. 5847012), is acknowledged.

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Reactions of Transition-Metal Carbonyl Anions with Dioxygen in the Gas Phase

Kelley Lane, Larry Sallans, and Robert R. Squires*

Department of Chemistry, Purdue University
West Lafayette, Indiana 47907

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Molecular metal oxides have provided a key source of fundamental information regarding oxidation-state stabilities,[1-3] metal-oxygen bonding,[4-8] combustion,[9] corrosion processes,[10] and catalytic oxidation mechanisms.[8,11,12] Mononuclear transition-metal polyoxides and their partially ligated derivatives are often kinetically unstable as discrete molecules, however, and methods involving extremes of temperature and/or fast spectroscopic probes are frequently necessary for their formation and characterization.[13-27] We wish to report here the formation of several novel

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Table I. Reactions of Metal Carbonyl Anions with Dioxygen, 296 ± 2 K

$M(CO)_n^-$	k_{obsd}[a]	efficiency[b]	primary products (%)	terminal ions[c]
$Fe(CO)_4^-$	1.53	0.03	$Fe(CO)_2O^-$ (75) $Fe(CO)_3O_2^-$ (15) $Fe(CO)_3O^-$ (5) $Fe(CO)_2O_2^-$ (5)	$FeO_{2,3,4}^-$ $Fe(CO)_3O_2^-$
$Cr(CO)_5^-$	3.95	0.07	$Cr(CO)_3O^-$ (95) $Cr(CO)_3O_2^-$ (5)	$CrO_{2,3,4,5}^-$ $Cr(CO)_3O_2^-$
$Mo(CO)_5^-$	7.15	0.13	$Mo(CO)_3O_2^-$ (55) $Mo(CO)_4O_2^-$ (45)	$MoO_{3,4,5}^-$
$Mn(CO)_5^-$	<0.01	<0.0002		
$Co(CO)_4^-$	<0.01	<0.0002		

[a] In units of 10^{-11} cm^3 $molecule^{-1}$ s^{-1}. Sufficient quantities of SF_6 are added downstream of the ion source to scavenge free electrons that might otherwise ionize the metal carbonyls in the reaction region and cause erroneously low rate measurements. [b] Efficiency = $k_{obsd}/k_{Langevin}$: Su, T.; Bowers, M. T. in "Gas Phase Ion Chemistry", Bowers, M. T., Ed.; Academic Press, New York, 1979; Chapter 3. [c] Secondary product ions and relatively unreactive primary product ions appearing in the mass spectra at high O_2 flow rates.

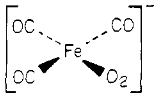
examples of molecular metal oxide anions produced at room temperature in the gas phase by reactions of transition metal carbonyl ions with dioxygen (eq 1).

$$M(CO)_n^- \xrightarrow{O_2} M(CO)_xO_y^- \tag{1}$$

$$M = Fe, Cr, Mo, Mn, Co; n = 4, 5; x = 0\text{–}4; y = 1\text{–}5$$

Our experiments have been carried out at 296 ± 2 K in a flowing afterglow apparatus recently constructed in our laboratories.[28,29] The negative metal ions $Fe(CO)_4^-$, $Cr(CO)_5^-$, $Mo(CO)_5^-$, $Mn(CO)_5^-$, and $Co(CO)_4^-$ are produced by electron impact on the parent carbonyls $Fe(CO)_5$, $Cr(CO)_6$, $Mo(CO)_6$, $Mn_2(CO)_{10}$, and $Co_2(CO)_8$, respectively.[30] A fast flow of helium (F(He) = 150 STP cm^3 s^{-1}; P(He) = 0.3 torr) carries ions formed in the source region through a 100 cm × 7 cm i.d. flow reactor where they interact with O_2 added to the system via fixed or moveable inlets. The plasma is sampled into a downstream quadrupole mass spectrometer for mass analysis and ion detection.

The 17-electron metal carbonyl radical anions $Fe(CO)_4^-$, $Cr(CO)_5^-$, and $Mo(CO)_5^-$ each undergo a relatively slow reaction with $^3\Sigma^-O_2$ to yield an interesting array of mononuclear metal carbonyl oxides and polyoxide anion products (eq 1). Primary product ion distributions and bimolecular rate coefficients[31,32] have been determined for these reactions and are summarized in Table I. Increasing the O_2 flow rate exposes the evolution of several secondary polyoxide product ions and the eventual emergence of slower reacting sets of "terminal" ions listed in the last column of the table. No ionic products of higher nuclearity are detected. This suggests either a lack of condensation reactions between the oxides and their parent neutral carbonyls or facile oxidative cleavage of any such condensate ions as they form under the conditions of the experiment. The differences in primary product selection and secondary oxidations exhibited by the three reactants are interesting. Whereas $Fe(CO)_4^-$ and $Cr(CO)_5^-$ react mainly by O_2 addition followed by loss of both CO and CO_2,[33] the second-row carbonyl anion $Mo(CO)_5^-$ produces primarily dioxide products in which one or two CO ligands have been expelled. A greater preference for accumulation of metal–oxygen bonds in the molybdenum ions relative to iron and chromium could be viewed as a manifestation of the generally stronger oxygen bond strengths which are known for molybdenum compounds.[2,34] Each of the three reactive ions forms a tricarbonyl dioxide species as a primary product. In the case of iron and chromium, these species appear to be relatively inert toward further oxidation by O_2; i.e., their detected abundance increases monotonically with increasing O_2 flow while all other primary product ions react away. This is in contrast to both $Mo(CO)_3O_2^-$ and $Mo(CO)_4O_2^-$, which fairly rapidly give way to MoO_x^- ions with increasing O_2 flow. While we can only speculate as to the structures of these ions, the formulations depicted below are particularly attractive candidates.



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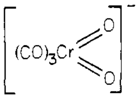
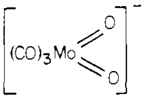


2



3

In **1** a relatively favored (albeit rare) d^8 square-planar configuration[3] can be achieved by binding O_2 as a superoxo[4] ligand, while **2** and **3** are chosen by analogy with the recently reported structures for matrix-isolated $CrO_2(CO)_2$[20] and MoO_2,[24] respectively.

The dioxide anions FeO_2^-, CrO_2^-, and MoO_2^- have been observed previously in high-temperature solid solutions[35,36] and sputter ion sources.[37,38] Several of the higher polyoxide ions such as CrO_3^-, CrO_5^-, MoO_4^-, MoO_5^-, and FeO_4^- are unusual, however, and must involve either rare oxidation states[1,3,39] and/or oxygen bonding modes[4-8] or, alternatively, may exist as loosely bound anion–O_2 clusters (e.g., $MO_x^-{\cdot}O_2$). This latter possibility appears unlikely, however, since in no case do any of the polyoxide anions undergo neutral O_2-switching reactions in the presence of polar, hydrogen-bonding reactants such as H_2O.

The radical nature of the primary oxidation mechanism is illustrated by the lack of reactivity exhibited by the closed-shell, 18-electron species $Mn(CO)_5^-$ and $Co(CO)_4^-$. The decay of these ion signal intensities is negligible even with very high O_2 flow rates in the reactor, thereby setting an upper limit to the rate constants of $\lesssim 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}. Since metal–oxygen bond formation is likely to be exothermic,[40] this effect must be kinetic in origin

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and is consistent with the larger activation barriers that frequently impede association reactions between singlets and triplets.[41,42] It is noteworthy in this regard that the reactions of $^3O_2$ with the odd electron, radical anions $Fe(CO)_4^-$, $Cr(CO)_5^-$, and $Mo(CO)_5^-$ are surprisingly slow (Table I), despite the favorable energetics and kinetic factors that might otherwise be expected for their direct reaction. The origin of this effect may lie in unfavorable spin localization requirements or inaccessible spin states of the product polyoxide ions and is presently under investigation. We are also currently examining the gas-phase reactions of the polyoxide ions with a series of neutral substrates and will report these results in a future publication.

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Bimetallic Solvated Metal Atom Dispersed Catalysts. New Materials with Low-Temperature Catalytic Properties

Kenneth J. Klabunde* and Yuzo Imizu[†]

Department of Chemistry, Kansas State University
Manhattan, Kansas 66506

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During 1974–1976 we reported the first examples of solvated metal atom dispersion (SMAD).[1-3] In this process metal atoms such as Mg, Ni, Co, Fe, etc. are solvated at low temperature in toluene or some other appropriate solvent, and upon warming metal atom nucleation begins, but this nucleation process (cluster growth) competes with a reaction channel where the growing clusters react with the host solvent.[4] These reactions, even with alkanes, can occur extensively as low as 140 K (−130 °C).[5] This observation in itself indicates that these small growing clusters are *fundamentally different and more reactive* than clean metal surfaces.[5] Appropriate theoretical rationale for this variant behavior are not currently available.

These growing clusters incorporate carbonaceous fragments and stabilize as amorphous "pseudoorganometallic" powders, which represent a special new class of materials. We have provided many examples showing where these materials behave as novel heterogeneous catalysts.[6] Contrary to popular current thought, the incorporated carbonaceous fragments do not poison but instead *aid* the catalytic action[7] and apparently even provide a better means of attachment of the metal particles to catalyst support surfaces.[6c]

In our earlier paper we also suggested that the SMAD procedure would be useful for the preparation of bimetallic particles.[3] Herein we report our initial results in this area and show that Mn–Co pseudoorganometallic particles possess catalytic activities that allow alkene hydrogenation at −60 °C at diffusion-controlled rates, which represents considerably increased activity over all other SMAD monometallic catalysts we have prepared, including Ni, Co, Fe, Mn, and Cr.[8]

Table I. Initial Reaction Rates for 1-Butene Isomerization, 1-Butene Hydrogenation, and 1,3-Butadiene Hydrogenation over Monometallic and Bimetallic SMAD Catalysts

		initial rates, molecule/(M atom s)		
catalyst[b]	atom %[c]	isom $1\text{-}C_4{}'$	hydrog $1\text{-}C_4{}'^{e}$	hydrog $1.3\text{-}C_4{}''^{f}$
2.6% Co–1.5% Fe	39.4	0.017	0.44^g	$0.14\ (0.41)^h$
1.5% Co–3.4% Fe	70.5	0.0096	0.0063	$0.029\ (0.96)^h$
2.4% Co–6.8% Fe	74.9	0.00087	0.00016	$0.0049\ (0.96)^h$
4.1% Co–0.1% Mn	2.5	0.018	0.35^g	$0.18\ (0.57)^h$
3.6% Co–0.8% Mn	19.3	0.084	0.45^g	
2.0% Co–1.1% Mn	37.6	0.018	0.79^g	
3.3% Co–2.6% Mn	45.8	0.024	0.53^g	
3.4% Co–3.3% Mn	51.0	0.021	0.50^g	$0.083\ (0.56)^h$
1.7% Co–5.1% Mn	76.3	0.016	0.016	$0.0053\ (0.95)^h$
3.6% Co–0.7% Cr	18.1	0.0034	0.0051	$0.011\ (0.96)^h$
2.0% Co–2.2% Cr	55.5	0.00022	0.0028	$0.011\ (0.94)^h$
0.6% Co–3.7% Cr	87.5	0	0.0047	$0.011\ (0.95)^h$
4.7% Fe		0.00053	0.00022	$0.0048\ (0.97)^h$
2.3% Co		0.0063	0.029	$0.012\ (0.98)^h$
3.4% Mn		0	0.000013	$0.00030\ (1.0)^h$
3.8% Cr		0	0	0

[a] Based on 100% Co dispersion neglecting second metal contribution. [b] SiO_2 support, wt %. [c] Atom % of second metal, not including support. [d] $P_{rea} = 30$ torr, without H_2, 253 K. [e] $H_2/HC = 1.67$, $P_{tot} = 80$ torr, 213 K. [f] $H_2/HC = 2$, $P_{tot} = 60$ torr, 273 K. [g] The rate was controlled by diffusion. [h] Ratios of butene to (butenes + butane).

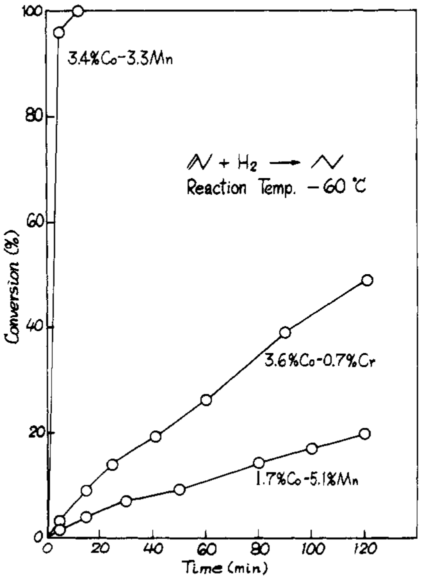

Figure 1. Effect of Mn addition on hydrogenation activity for a Co/SiO_2 SMAD catalyst.

An apparatus similar to those described previously[9] was constructed possessing four water-cooled copper electrodes, two $W\text{-}Al_2O_3$ metal vaporization crucibles, and two separate power supplies. Two metals were vaporized simultaneously as excess toluene solvent vapor was inletted. The liquid nitrogen cooled walls condensed the toluene and metal atoms into a frozen matrix. About 0.02–1.4 g of each metal and 100 mL of toluene were used in each experiment, which lasted about 2 h.

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