distortion from a "conventional" Fe_4S_4 core.

A cation of the same stoichiometry and with PF_6^- as counterion has been reported by Vergamini and Kubas.[7] This, however, has been obtained by using a different pathway from ours, namely by *slow* S abstraction, by air oxidation, from $Fe_4S_6Cp_4$ to form $[Fe_4S_5Cp_4]^{2+}$, which is then added to the neutral species $Fe_4S_5Cp_4$ to give the monocation. Moreover, these authors propose, on the basis of NMR studies, a different structure of the Fe_4S_5 core, with the S_2 group bound to only two iron atoms. At the present state of knowledge, one cannot assume whether these two cations do have the same structure or not.

When examined in frozen CH_3CN solutions at 4.2 K and at fairly low concentration (<1 mmol/L), complex I exhibits an EPR rhombic spectrum of $S = {}^1/_2$ type, having principal g values at 2.188, 1.999, and 1.968. The temperature dependence of the spectrum resembles that of Fe_4S_4 sites in both proteins and model compounds,[22] and the signals are totally unobservable above 140 K, indicating a rapid electronic spin relaxation rate. A concentration dependence is also observed: when the cluster concentration is increased up to 10 mmol/L, the signals are broadened, indicating an extensive intercluster magnetic interaction. The Mo(V) anion is evidenced by the presence at low T (4.2–150 K, 5–10 mmol/L) of three signals having $g_x = 1.913$, $g_y = 1.939$, and $g_z = 1.978$ (the latter is best visible at 150 K, when the cluster signals have disappeared). At higher T (190 K) a strong isotropic signal ($S = {}^1/_2$) is visible at $g = 1.942$ $(=(g_x + g_y + g_z)/3)$ with $A(^{95,97}Mo) = 44$ G, which is consistent with the presence of a monomeric Mo(V) species.

Preliminary Mössbauer experiments on I in the solid state at 4.2 K, without an external magnetic field, display one doublet with isomer shift (IS) of 0.31–0.35 mm/s (vs. Fe metal at 300 K), quadrupole splitting (QS) of 1.075 mm/s and a line width of 0.40 mm/s. When the temperature is increased, from 1.4 to 77 K, the hyperfine parameters do not change.

These values are intermediate between the parameters corresponding to Fe^{2+} and Fe^{3+} ions with tetrahedral coordination and indicate a charge delocalization in the Fe_4S_5 core. The IS magnitude has been shown[23] to follow a nearly linear correlation with the average oxidation state of the iron atoms. This implies that in our case we have $Fe^{2.75+}$ (3 Fe^{III}, 1 Fe^{II}), although the spectra show no evidence of nonequivalent Fe atoms. The line-width invariance when changing the temperature indicates that, even at $T = 1.4$ K, the Mössbauer spectrum is not magnetically split. This observation confirms that this magnetic cluster, with a magnetic moment of $\mu = 2.62$ at 5 K and in the solid state, has a very short electronic spin relaxation time as compared with the Lazmoz nuclear precession, because of spin–spin interaction between the clusters.

Electron counting arguments are in support of assigning different formal oxidation states to the Fe centers. Assuming each Cp^- contributes six electrons to the metal, each S^{2-} six electrons, and the S_2^{2-} eight electrons, then, to derive an 18-electron configuration at each metal center (71 electrons for $[Fe_4S_5Cp_4]^+$), we assign oxidation states of 3 Fe^{3+} and 1 Fe^{2+}. This observation, joined to the EPR results giving a $g_{av} > 2$, suggests the presence of a $[Fe_4S_5]^{3+}$ type core in compound I, which can therefore be considered as a minimal model for $Hipip_{ox}$.[22]

Detailed magnetic susceptibility and Mössbauer studies are currently under way to gain information about spin–relaxation processes and to try to visualize any magnetic inequivalence of the structurally different Fe(3) site.

Registry No. I, 89016-76-2; $Fe_4S_6Cp_4$, 72256-41-8; $MoOCl_3(thf)_2$, 20529-42-4; Fe, 7439-89-6.

Supplementary Material Available: Tables of all positional and thermal parameters, additional interatomic distances and bond angles, and observed and calculated structure factors for compound I (21 pages). Ordering information is given on any current masthead page.

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Unusual Stabilization of Formylmetal Complexes

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Summary: The exceptional stabilization of a variety of transient formylmetal complexes can be achieved by the judicious addition of tri-*n*-butyltin hydride and other hydrogen donors. The saturation effect of these additives (illustrated in Figure 1) dictates that alternative pathways involving nonchain decompositions must be identified in addition to the efficient radical-chain mechanism demonstrated in the previous study.

Metal catalysis of carbon monoxide reduction has recently centered around formylmetal complexes as one of the prime intermediates along the reaction pathways.[1] Although a variety of formylmetal species has been generated by the action of various hydridic reducing agents on metal carbonyls of different structural types,[2] their role as intermediates in the catalytic hydrogenations of carbon monoxide has not been established owing to their apparent instabilities. As part of our interest in the reduction of metal carbonyls,[3] we recently noted a highly efficient radical-chain mechanism for the conversion of the formylrhenium complex *cis*-$(OC)_5ReRe(CO)_4CHO^-(Bu_4N)^+$ to the corresponding hydridorhenium complex, i.e.,[4]

$$(OC)_5ReRe(CO)_4C(=O)H^- \rightarrow (OC)_5ReRe(CO)_4H^- + CO \quad (1)$$

The catalytic turnover number in this system is very high (>400), and the radical chain could be triggered thermally with azo compounds and by photochemical or electro-

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[2] For a review, see: Gladysz, J. A. *Adv. Organomet. Chem.* **1982**, *20*, 1.

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Table I. Stabilization of the Formylchromium Complex $Cr(CO)_5CHO^-$ by Various Additives[a]

additive	n[b]	yield,[c] %	τ,[d] min	decomposition products (% yield)
none		70	39	$Cr(CO)_5H^-$[e] (10), μ-H-$[Cr(CO)_5]_2^-$[f] (17)
γ-terpinene[g]	1	85	65	$Cr(CO)_5H^-$ (24)
	2	86	110	$Cr(CO)_5H^-$ (40)
	3	88	142	$Cr(CO)_5H^-$ (42)
	5	87	174	$Cr(CO)_5H^-$ (39)
dihydroanthracene[h]	1	85	80	$Cr(CO)_5H^-$ (15)
	2	86	123	$Cr(CO)_5H^-$ (34)
	3	85	139	$Cr(CO)_5H^-$ (42)
	5	88	160	$Cr(CO)_5H^-$ (41)
methoxy-1,4-cyclohexadiene[g]	1	82	104	$Cr(CO)_5H^-$ (24)
	2	85	118	$Cr(CO)_5H^-$ (37)
	3	88	122	$Cr(CO)_5H^-$ (42)
	5	88	138	$Cr(CO)_5H^-$ (43)
tri-*n*-butyltin hydride[g]	0.1	92	165	$Cr(CO)_5H^-$ (16)
	1	90	170	$Cr(CO)_5H^-$ (14)
	2	86	172	$Cr(CO)_5H^-$ (35)

[a] All experiments were carried out in degassed, sealed Pyrex tubes. The formyl complex was generated in situ by the addition of a 10% molar excess of K(*i*-PrO)$_3$BH (1 M solution in THF) to 1.0×10^{-1} M $Cr(CO)_6$ and the additive in THF. [b] Molar equivalents of additive present. [c] Yield of formylchromium complex $Cr(CO)_5CHO^-$ based on $Cr(CO)_6$ charged in the presence of additive. [d] Apparent half-life; see footnote 5. [e] Identified by its characteristic ^{1}H NMR resonance at −7.0 ppm.[6] [f] Identified by its characteristic ^{1}H NMR resonance at −19.5 ppm.[6] [g] *p*-Di-*tert*-butylbenzene used as the internal standard. [h] *p*-Dimethoxybenzene used as the internal standard.

chemical techniques. Also of importance, the facile chain process for eq 1 was effectively interrupted by the addition of dihydroanthracene, which is a known radical inhibitor.

We now wish to demonstrate how the identification and annhilation of the radical-chain pathways provide direct access to the study of other relevant modes for the decomposition of formylmetal complexes. Accordingly in this study we have employed a variety of agents (i.e., retarders) in an attempt to intercept the chain-propagating radicals and thus prolong the half-life[5] (stability) of the formylmetal complexes.

We first examined the stabilization of the formylchromium complex $Cr(CO)_5CHO^-$, since it can be readily generated in >70% yield[6] from chromium hexacarbonyl and a slight stoichiometric excess (10%) of potassium tris(1-methylethoxy)borohydride (K(*i*-PrO)$_3$BH) in tetrahydrofuran (THF) solution.[7] Formed under these conditions, it decomposed with an apparent half-life of 39 min at 25 °C to afford the hydride $Cr(CO)_5H^-$ and the μ-hydride $(OC)_5CrHCr(CO)_5^-$ in 10% and 17% yields, respectively, among other unidentified products.[8] However, the half-life of $Cr(CO)_5CHO^-$ *increased sharply* in the presence of additives such as tri-*n*-butyltin hydride, γ-terpinene, methoxy-1,4-cyclohexadiene, and dihydroanthracene, as listed in Table I.[9] Moreover, the half-life of the formylchromium complex also reaches a limiting value beyond which no added retarder has any effect. Indeed the results in Figure 1 show that the limiting values of the half-life are more or less the same for all retarders.[10] Thus we deduce that the plateau τ ~ 170 min represents a limit beyond which there exists only nonchain pathways for decomposition of the formyl complex (and common to the system).

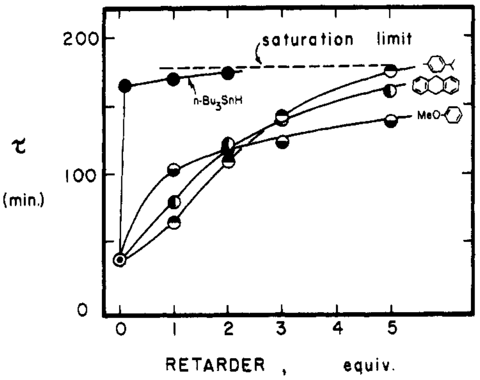

Figure 1. Variation of the stability (half-life) of the formylchromium complex $Cr(CO)_5CHO^-$ in the presence of various amounts of retarders: γ-terpinene ◒, dihydroanthracene ◑, methoxy-1,4-cyclohexadiene ◓, tri-*n*-butyltin hydride ●.

Examination of the results in Table I clearly reveals tri-*n*-butyltin hydride to be the most effective additive.[11] Indeed the maximum stabilization (i.e., τ ~ 165 min) for the formylchromium complex $Cr(CO)_5CHO^-$ was readily attained with even less than *0.1 equiv* of *n*-Bu_3SnH.

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(5) The half-life τ as used here refers to the time required for 50% decomposition under the experimental conditions as stated.

(6) Yields were determined spectrally (typically described by previous workers[7,14]) by the integration of the proton resonances in the ^{1}H NMR spectra using either *p*-di-*tert*-butylbenzene or *p*-dimethoxybenzene as internal standards.

(7) Casey, C. P.; Neumann, S. M. *J. Am. Chem. Soc.* **1976**, *98*, 5395.

(8) (a) Analysis of the decomposition products showed that the yield of the hydride $Cr(CO)_5H^-$ increased with increasing amounts of retarder. By contrast, the formation of the μ-hydride $(OC)_5CrHCr(CO)_5^-$ was singularly inhibited by the presence of these retarders.[8b] Thus the conversion of the formylchromium complex $Cr(CO)_5CHO^-$ to the corresponding hydride species $Cr(CO)_5H^-$ is consistent with the radical-chain mechanism outlined previously.[4] However, such a homolytic pathway cannot be the sole route by which the formyl complex decomposes, since the yield of $Cr(CO)_5H^-$ reaches a plateau of ~45% which is independent of the concentration and the structure of the retarder. (b) Since it is known that the μ-hydride is formed from the monohydride on standing,[8c] the pronounced effect of the retarders suggest that this conversion may also proceed via radical intermediates. (c) Darensbourg, M. Y.; Deaton, J. C. *Inorg. Chem.* **1981**, *20*, 1644.

(9) (a) Borohydrides and related hydridic reducing agents used in the synthesis of formylmetal complexes are known to participate in radical reactions.[9b] Thus the values of τ observed in the absence of retarders may already represent partially retarded processes. If so, the actual radical-chain process for formylmetal decomposition may be even more efficient than indicated by τ in the absence of retarder. (b) See, e.g.: Ashby, E. C.; Goel, A. B.; DePriest, R. N.; Prasad, H. S. *J. Am. Chem. Soc.* **1981**, *103*, 973. Michaud, P.; Astruc, D.; Ammeter, J. H. *Ibid.* **1982**, *104*, 3755. Wagner, W. R.; Rastetter, W. H. *J. Org. Chem.* **1983**, *48*, 294. Baban, J. A.; Brand, J. C.; Roberts, B. P. *J. Chem. Soc., Chem. Commun.* **1983**, 315. Beckwith, A. J.; Goh, S. H. *Ibid.* **1983**, 905. Chung, S. K. *J. Org. Chem.* **1980**, *45*, 3513, for some leading references.

(10) The quality of the half-life values[5] is sufficient to indicate a common convergence limit in Figure 1.

(11) Tri-*n*-butyltin hydride is also known to be very active with organic radicals. See Lusztyk et al. (Lusztyk, J.; Lusztyk, E.; Maillard, B.; Lunazzi, L.; Ingold, K. U. *J. Am. Chem. Soc.* **1983**, *105*, 4475) for some leading references.

Table II. Stabilization of Various Formylmetal Complexes by n-Bu_3SnH[a]

formyl complex	yield,[b] %	Bu_3SnH, equiv	^1H NMR[c]	τ,[d] min	decomposition products (% yield)
$Cr(CO)_5CHO^-K^+$	70		15.2	39	$Cr(CO)_5H^-$[e] (10), μ-H-$[Cr(CO)_5]_2^-$[f] (17)
$Cr(CO)_5CHO^-K^+$	92	0.1	15.1	165	$Cr(CO)_5H^-$ (16)
$Cr(CO)_5CHO^-K^+$	90	1	15.1	170	$Cr(CO)_5H^-$ (14)
$Cr(CO)_5CHO^-K^+$	86	2	15.1	172	$Cr(CO)_5H^-$ (35)
$W(CO)_5CHO^-K^+$	74		15.9	16	μ-H-$[W(CO)_5]_2^-$[g] (17)
$W(CO)_5CHO^-K^+$	76	1	15.8	28	$W(CO)_5H^-$[h] (50)
$W(CO)_5CHO^-K^+$	76	2	15.8	60	$W(CO)_5H^-$ (48)
$(CH_3CO)Re(CO)_4CHO^-K^+$	87	2	15.7	78	$(CH_3CO)Re(CO)_4H^-$[n] (32)
$Re(CO)_4BrCHO^-Li^+$[m]	58	1	14.95	130	*i*
$Mn(CO)_3(PPh_3)_2CHO$[j]	77	2	13.45	30	$HMn(CO)_3(PPh_3)_2$[k] (15)
$Mo(CO)_5CHO^-K^+$[l]	40	2	15.4	<10	*i*
$Mn_2(CO)_9CHO^-Li^+$	p	2			*i*

[a] The formylmetal complexes were formed either by the addition of $K(i\text{-}PrO)_3BH$ (1 M in THF) or $Li(C_2H_5)_3BH$ (1 M in THF) to a 1.0×10^{-1} M solution of the parent metal carbonyl and the appropriate amount of n-Bu_3SnH in THF. Experiments performed in degassed, sealed NMR tubes. [b] The yields refer to the conversion of the metal carbonyl to the formylmetal complex. [c] Formyl resonance relative to Me_4Si. [d] Apparent half-life; see footnote 5. [e] Identified by its characteristic ^1H NMR resonance, −7.0 ppm.[6] [f] Identified by its characteristic ^1H NMR resonance, −19.5 ppm.[6] [g] Identified by its characteristic ^1H NMR resonance, −12.5 ppm.[6] [h] Identified by its characteristic ^1H NMR resonance, −4.5 ppm.[6] [i] No hydride resonances could be observed between 0 and −30.0 ppm. [j] The formyl complex was formed by the addition of a slight excess of $Li(C_2H_5)_3BH$ (1 M in THF) to 2×10^{-2} M $Mn(CO)_4(PPh_3)_2^+\ PF_6^-$ in CH_2Cl_2. [k] Identified by its characteristic ^1H NMR spectrum (−7.2 ppm, t, J = 33 Hz). [l] In the absence of n-Bu_3SnH, the formyl complex was formed in 17% yield. [m] In the absence of n-Bu_3SnH, $Re(CO)_5H$ (−5.2 ppm) was formed exclusively in 85% yield. [n] Identified by its characteristic ^1H NMR spectrum (−4.7 ppm).[12] In the absence of Bu_3SnH, the hydride was formed in 94% yield. [p] Not stable at room temperature.

Further addition of the tin hydride had no effect on the half-life, in striking accord with the saturation limit described in Figure 1.

The efficacy of the tin hydride to effectively inhibit the radical-chain process, we believe, has an important bearing on the role of other metal hydrides to act in a similar capacity in *catalytic* systems. Accordingly we examined the stabilization by tributyltin hydride of a variety of other formylmetal complexes presented in Table II. Thus the formyltungsten complex $W(CO)_5CHO^-$ can be generated in 74% yield,[7] and it has an apparent half-life of 16 min at 25 °C to afford the μ-hydride $(OC)_5WHW(CO)_5^-$ as the principal decomposition product. In the presence of n-Bu_3SnH, the half-life of $W(CO)_5CHO^-$ is prolonged substantially, and the principal product is the tungsten hydride $W(CO)_5H^-$, as given in Table II. Similarly the half-life of the mixed formylacetylrhenium complex[12] $CH_3CORe(CO)_4CHO^-$ can be increased from 8 min to 78 min in the presence of 2 equiv of n-Bu_3SnH. Even haloformylrhenium complexes such as $BrRe(CO)_4CHO^-$, which are unstable at room temperature,[13] could be stabilized by 2 equiv of n-Bu_3SnH (τ 130 min at 25 °C). Likewise, the neutral formyl complex $Mn(CO)_3(PPh_3)_2CHO$,[14] which decomposes readily at 0 °C, could be seen at room temperature (τ 30 min) in the presence of 2 equiv of n-Bu_3SnH.

It is noteworthy that there are some formylmetal complexes such as $(OC)_5MnMn(CO)_4CHO^-$[15] and $Mo(CO)_5CHO^-$[7] whose stabilities are not noticeably affected by the presence of n-Bu_3SnH. Since these formyl complexes do not afford the corresponding hydrides as decomposition products, we infer that the radical-chain mechanism is mainly applicable to those formylmetal complexes which are readily converted to their hydride derivatives. However there are other formylmetal complexes such as $CH_3CORe(CO)_4CHO^-$ and $BrRe(CO)_4CHO^-$ (vide supra), which are stabilized but afford the corresponding carbonylmetal hydrides in considerably reduced yields in the presence of n-Bu_3SnH. Clearly the isolation and identification of the products formed under these conditions will provide important insights into the nonchain processes for the decomposition of formylmetal species.

Our results thus indicate that a multiplicity of pathways are available for the reaction of formylmetal intermediates. In particular we have identified the existence of additional nonchain pathways by which formylmetal intermediates can disappear.[16] The delineation of these molecular processes (with the aid of retarders described in this study) will doubtlessly lead to additional insight into the role of formylmetal intermediates in the catalytic reduction of carbon monoxide.

Acknowledgment. We wish to thank the National Science Foundation and the United States–France (NSF–CNRS) cooperative program for financial support.

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(12) Darst, K. P.; Lukehart, C. M. *J. Organomet. Chem.* **1979**, *171*, 65.

(13) See ref 12. Note that $BrRe(CO)_4CHO^-$ has been stabilized by the addition of LiBr. The decomposition products will be reported at a later time.

(14) Tam, W.; Lin, G. Y.; Gladysz, J. A. *Organometallics* **1982**, *1*, 525.

(15) Tam, W.; Marsi, M.; Gladysz, J. A. *Inorg. Chem.* **1983**, *22*, 1413.

(16) See, e.g., ref 1e and: Davies, S. G.; Hibberd, J.; Simpson, S. J. *J. Chem. Soc., Chem. Commun.* **1982**, 1404. Compare also: Lin, Y. C.; Milstein, D.; Wreford, S. S. *Organometallics* **1983**, *2*, 1461.

(*R*,*R*)-2,3-Butanediol as Chiral Directing Group in the Synthesis of (αS)-α-Chloro Boronic Esters

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Summary: (*R*,*R*)-2,3-Butanediol dichloromethaneboronate is a convenient reagent for attaching a chiral carbon to a Grignard or lithium reagent via zinc chloride catalyzed rearrangment of the intermediate borate complex, which yields (αS)-α-chloro boronic esters with