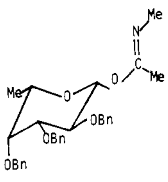
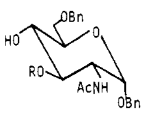
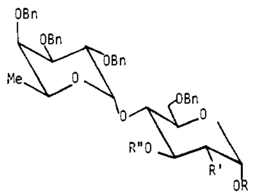


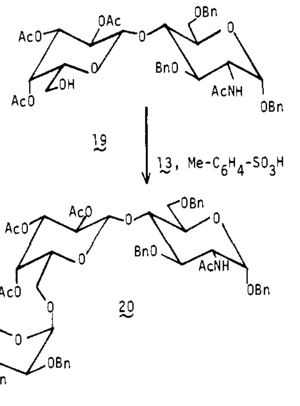
13

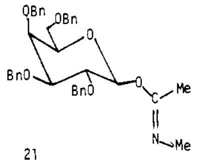


14 R = Bn
15 R = A



16 R = Me, R' = OBn, R" = Bn
17 R = Bn, R' = NHAc, R" = Bn
18 R = Bn, R' = NHAc, R" = A





21

Bn = $CH_2C_6H_5$
A = $CH_2\text{-}CH{=}CH_2$

stability and its ease of preparation from hemiacetal **11**, the imidate **13** appears as an efficient α-L-fucosylating agent. Further use for the syntheses of blood group substances is now under way in our laboratory.

Finally, 1-*O*-(*N*-methyl)acetimidyl-2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranose (**21**) was used to prepare the protected disaccharide **10** (74%) as a glass, $[\alpha]^{20}{}_D$ +33° (*c* 1.1, $CHCl_3$).[15]

The examples reported herein prove that this novel approach is of wide applicability for the preparation of a wide variety of di- and oligosaccharides.

References and Notes

(1) Research supported by Centre National de la Recherche Scientifique, Institut National de la Santé et de la Recherche Médicale and Délégation Générale à la Recherche Scientifique et Technique (ASCO, Grant No. 74 7 0973 and 75 1 1364).

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(3) This chloride was conveniently prepared in one step (85%) from commercially available 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranose (Pfanstiehl, Waukegan, U.S.A.), under the agency of dimethylchloroformiminium chloride (prepared from dimethylformamide and phosphorus pentachloride according to ref 4).

(4) H. H. Bosshard, R. Mory, M. Schmid, and Hch. Zollinger, *Helv. Chim. Acta*, **42**, 1653 (1959).

(5) All new compounds gave correct microanalyses and exhibited IR and NMR spectral characteristics that were in accord with their structures.

(6) See J. R. Pougny and P. Sinaÿ, *Tetrahedron Lett.*, 4073 (1976), for the syntheses of some aromatic imidates.

(7) Except in acetonitrile where a majority of β-glucoside was obtained, presumably through a nitrilium intermediate.[6] Benzene was finally selected as a standard solvent, but the nature of the solvent was not optimized in each specific case.

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(9) When methyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranoside was partnered with 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl bromide according to Lemieux et al.,[2c] no disaccharide was formed. In general many difficulties have been experienced with the glycosylation of the 4-hydroxyl group of glucopyranoside derivatives and it is only recently that a practical synthesis (44%) of a maltose derivative has been described.[2d]

(10) A value of +174° (*c* 0.9, water) was reported for pure methyl α-maltoside: W. E. Dick, Jr., D. Weisleder, and J. E. Hodge, *Carbohydr. Res.*, **18**, 115 (1971).

(11) In this case, ~15% of the β anomer was present in the reaction mixture, as shown by GLC. The pure β anomer was isolated in small amount after column chromatography, mp 133–133.5 °C, $[\alpha]^{20}{}_D$ +17.1° (*c* 0.42, $CHCl_3$).

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(15) In the case of the three amorphous disaccharides **3**, **4**, and **10**, no β anomer was detectable using ^{1}H NMR spectroscopy.

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Stepwise Reduction of the Carbon–Nitrogen Triple Bond of Acetonitrile on the Face of a Triiron Nonacarbonyl Cluster

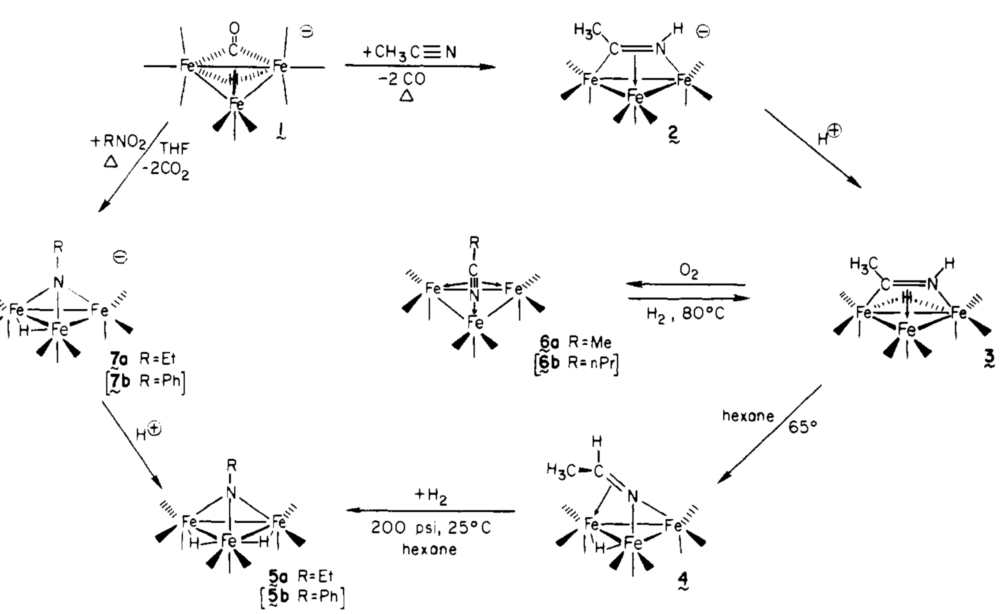
Sir:

The use of transition metal clusters as homogeneous catalysts[1] and stoichiometric reagents[2] is currently of great interest.[3] Metal atom clusters permit a greater variety of interactions with substrates than is possible in mononuclear complexes. Some examples can be cited for the cluster chemistry of iron,[4a,b] but an even richer field has been found for ruthenium and osmium.[4b,c,5] This greater diversity of interactions is also believed to be responsible for the ability of clusters to carry out reactions which mononuclear species generally can not, such as the reduction of triple bonds.[3b] We report here the preparation of a unique series of complexes (Scheme I) which clearly delineate a sequence for the reduction of the carbon-nitrogen triple bond of an organic nitrile on the face of an $Fe_3(CO)_9$ cluster.

In an attempt to extend our studies of hydridocarbonyl cluster chemistry[6] to that of the more common metals we treated $W(CO)_5I^-$ with $Fe_2(CO)_8{}^{2-}$ in refluxing acetonitrile. The resulting anion mixture (later shown to contain **2**)[7a] was acidified and the neutral product thus obtained was analyzed by mass spectrometry. Surprisingly, it contained no tungsten, but it did contain the elements of a molecule of acetonitrile. Spectroscopic data[7b] indicated structure **3** which has been confirmed by an x-ray determination.[8] The tungsten byproduct was determined to be $W(CO)_3(CH_3CN)_3$. We have subsequently found that anion **2** is also formed by the base disproportionation reaction[9] of $Fe(CO)_5$ in moist acetonitrile, presumably via $HFe_3(CO)_{11}{}^-$ (**1**) (vide infra). Some $HFe(CO)_4{}^-$ as well as iron metal also forms. The $HFe(CO)_4{}^-$ decomposes when sodium iodide is included in the reaction mixture, thereby facilitating workup.[10] The only apparent reference to acetonitrile-induced base disproportionation of $Fe(CO)_5$ is a patent claiming $Fe(CO)_5$ as a catalyst precursor for the hydrogenation of nitriles to amines (500–5000 psi H_2, 100–300 °C).[11] The existence of metal carbonyl infrared spectral changes was noted (but not documented) in that work during preparation of the catalyst from $Fe(CO)_5$ in refluxing acetonitrile.

The neutral product $HFe_3(CO)_9(CH_3C{=}NH)$ (**3**) is slowly air oxidized in solution to give $Fe_3(CO)_9(CH_3C{\equiv}N)$ (**6a**)[12] in 20% yield. (The remaining iron can be approximately accounted for as $Fe(CO)_5$ and iron oxide.) Significantly, **6a** could not be prepared directly from either $Fe_3(CO)_{12}$ or $Fe_2(CO)_9$ and acetonitrile. It (**6a**) can, however, be hydrogenated back

Scheme I



to 3 at 1 atm pressure in refluxing cyclohexane. As expected (vide infra), **4** and **5a** are also formed under these conditions. Since compound **6a** did not give crystals suitable for x-ray work, a propyl derivative **6b** was prepared[13] whose structure[14] is analogous to that of the isoelectronic acetylide complex $HRu_3(CO)_9(C{\equiv}CR)$.[15]

A compound of the same composition (mass spectroscopy) as **3** can be isolated in 4% yield from the original preparations[10] which is assigned structure **4** based on spectral data, especially ^1H NMR.[16,17] This complex is an isomer of **3** and can in fact be prepared by the irreversible isomerization of **3** (with ~50% decomposition) in refluxing hexane. The *N*-iminyl (or alkylidenimino) bonding mode observed in **4** is thus thermodynamically more stable than the *C*-iminyl bonding mode found in **3**. Analogous 1,1 and 1,2 isomeric forms of isoelectronic hydrocarbon complexes, i.e., $H_2Os_3(CO)_9(C{=}CRH)$ and $H_2Os_3(CO)_9(RC{=}CH)$, are known for osmium and ruthenium[4,5] but, unlike the present case, these isomers do not interconvert.

Treatment of **4** with hydrogen gas (200 psi, room temperature) results in clean conversion to $H_2Fe_3(CO)_9(NCH_2CH_3)$ (**5a**).[20,21] This step completes the reduction of the carbon-nitrogen triple bond on the $Fe_3(CO)_9$ cluster starting from either **1** or **6**. Scheme I thus constitutes one of the clearest examples to date of the chain of events occurring on a cluster surface leading to the extensive transformation of an organic substrate. Although isoelectronic hydrocarbon analogues of most of the complexes in Scheme I are known for heavier metal (Ru and Os) clusters, no single interconversion scheme has yet been reported equivalent to the one demonstrated here; such a scheme, however, can be constructed from the separate reports.[23] In addition, Scheme I may serve as a model for the mechanism of the previously cited[11] $Fe(CO)_5$-catalyzed hydrogenation of nitriles to amines; iron metal ubiquitous in this system might also participate in the reaction.

Scheme I also provides useful insights into stoichiometric reactions involving clusters, especially those of $HFe_3(CO)_{11}^-$ itself. Thus, **1** is known to reduce nitro compounds to amines under protic conditions.[2a,c] By repeating the reaction under aprotic conditions, we have obtained an anion (presumably $HFe_3(CO)_9(NPh)^-$, **7**) which gives complex **5b** on room temperature acidification. The preparation of **7** and **5b** and the observation of peaks due to free aniline in the mass spectrum of **5b**[24] make it likely that they are intermediates in the reduction of nitro compounds to amines by **1**.

One final important question raised by the current work has to do with the nature of the iron complex(es) that lead to the formation of anion **2**. Our observations to date strongly implicate $HFe_3(CO)_{11}^-$ as the primary precursor. In particular, **1** does react with acetonitrile to give **2** together with $HFe(CO)_4^-$. We interpret this as evidence for the competition between (a) Fe-H addition or nucleophilic attack by **1** on acetonitrile (followed by proton transfer from Fe to N in the latter case) to give **2** and (b) nucleophilic cleavage of **1** by acetonitrile to give $HFe(CO)_4^-$. (The two $Fe(CO)_4$ fragments thus generated could be recycled to **1** by the disproportionation reaction or could decompose to iron metal, a by-product in the synthesis of **2** by all routes.) In contrast, we can specifically rule out $HFe(CO)_4^-$, $Fe_2(CO)_8^{2-}$, and $HFe_2(CO)_8^-$ as the species responsible for the formation of **2**, owing to the nonreaction of the first two and the disproportionation of the third (to $HFe(CO)_4^-$ and **1**) under the reaction conditions. These data suggest that Fe-H addition or nucleophilic attack on the carbon-nitrogen triple bond may be subject to an unfavorable equilibrium constant as indicated by the lack of any product formation with $HFe(CO)_4^-$. For the triiron cluster **1**, however, the triple bond reduction would become irreversible when followed by loss of two CO groups and coordination of the organic ligand to give **2**. This may be one of the reasons for the greater effectiveness of clusters over mononuclear complexes in reactions involving potentially multidentate ligands.

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(8) (a) M. A. Andrews, C. B. Knobler, and H. D. Kaesz, Southern California Crystallography Meeting, May 3. 1977. Cell data: $P\bar{1}$, a = 9.276 (3), b = 9.190 (2), c = 9.099 (2) Å; α = 92.40 (2), β = 90.79 (2), γ = 83.45 (3)°; Z = 2; V = 770.0 (4) Å^3 at −158 °C. (b) A complex containing a substitutionally isomeric form of the *C*-iminyl ligand found in **3**, namely, $H_2Os_3(CO)_9(CH{=}NCH_3)$, has recently been obtained from the reaction of $Os_3(CO)_{12}$ with trimethylamine: C. C. Yin and A. J. Deeming, *J. Organomet. Chem.*, **133,** 123 (1977).
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(10) $Fe(CO)_5$ (10 mL), NaI (11 g), and undried, reagent grade acetonitrile (300 mL) were refluxed under nitrogen for 48 h. The solvent was evaporated and the residue treated sequentially with deaerated acetone (30 mL), phosphoric acid (40 mL), and water (50 mL). The resulting precipitate was extracted with aliquots of hexane and chromatographed on silica gel. Hexane eluted complex **4** (0.45 g, 4%) and hexane–dichloromethane (80:20) eluted complex **3** (1.2 g, 11%). All complexes described in this paper are deep red. Neutral complexes are air stable for hours in hexane solution and days in the solid state.
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(12) Spectral data for **6a:** ν_{CO} (cyclohexane) 2086 (w), 2037 (s), 2028 (vs), 2015 (s), 2001 (vw), 1993 (w), 1983 (w), 1974 cm^{-1} (vw); ν_{CN} (CCl_4) 1610 cm^{-1}; ^{1}H NMR ($CDCl_3$) τ 6.55 (s); mol wt 463 (mass spectrum, ^{56}Fe).
(13) Complex **6**b is obtained by the same sequence of reactions as used for the preparation of **6a** except butyronitrile was employed as the solvent for the initial base disproportionation of $Fe(CO)_5$.
(14) M. A. Andrews, C. B. Knobler, and H. D. Kaesz, unpublished work. Cell data: $P2_1/m$, a = 9.003 (1), b = 11.226 (2), c = 8.986 (2) Å; β = 101.33 (1)°; Z = 2; V = 890.6 (3) Å^3.
(15) G. Gervasio and G. Ferraris, *Cryst. Struct. Commun.*, **2,** 447 (1973).
(16) Spectral data for **4a:** ν_{CO} (cyclohexane)i)089 (w),8z051 (s),8z028 (vs),i)013 (s), 2001 (m), 1995 (w), 1972 cm^{-1} (w); ν_{CN} (CCl_4) ~1325–1464 cm^{-1}; ^{1}H NMR ($CDCl_3$) τ 3.55 (d of q, 1, J = 2.0, 5.0 Hz), 7.76 (d, 3, J = 5.0 Hz), 28.98 (d, 1, J = 2.0 Hz); mol wt 463 (mass spectrum, ^{56}Fe).
(17) The *N*-iminyl (–N=CHR) ligand is known in terminal and double bridging forms,[16] but the triply bridging form observed for **4** is thus far unique. Somewhat related are the complexes $HM_3(CO)_{10}(C{=}NMe_2)$ (M = Fe,[19a] Ru,[19b] Os[6b]) which contain the isomeric doubling bridging $-C{=}NR_2$ ligand.
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(20) Spectral data for **5**a: ν_{CO} (cyclohexane) 2099 (m–w), 2060 (s), 2036 (vs), 2031 (s), 2022 (w), 2003 (s), 1985 (m), 1972 cm^{-1} (w); ^{1}H NMR ($CDCl_3$) τ 5.17 (q, 2, J = 7.0 Hz), 8.28 (t, 3, J = 7.0 Hz), 32.45 (s, 2); mol wt 465 (mass spectrum, ^{56}Fe).
(21) The ruthenium[22a] and osmium[22b] analogues of **5b** have been prepared previously by hydrogenation of $Ru_3(CO)_{10}(NPh)$ and by metalation of aniline with $Os_3(CO)_{12}$, respectively.
(22) (a) E. Sappa and L. Milone, *J. Organomet. Chem.*, **61,** 383 (1973); (b) C. C. Yin and A. J. Deeming, *J. Chem. Soc., Dalton Trans.*, 1013 (1974).
(23) The reduction of acetonitrile according to Scheme I is partially paralleled by the reduction of acetylene on osmium.[5] Thus, $H_2Os_3(CO)_{10}$ reacts with $RC{\equiv}CH$ to give $HOs_3(CO)_{10}(CH{=}CHR)$ which on heating gives a mixture of $H_2Os_3(CO)_9(HCCR)$ and $H_2Os_3(CO)_9(C{=}CRH)$.[5b,d] The former of these is isostructural with **3**, the latter with **4**. Importantly no evidence for interconversion could be found[5b] in contrast to our results for **3** and **4**. To our knowledge, only the latter osmium isomer (R = H) can be hydrogenated to give $H_3Os_3(CO)_9(CCH_3)$,[5c] isostructural with **5**, completing the reduction of the carbon–carbon triple bond. Similarly, we also find that isomer **4** hydrogenates much more readily than isomer **3**. The factors responsible for these differences and similarities between osmium and iron are not yet known, nor also is the feasibility of preparing the analogous acetylene-derived iron complexes.
(24) Peaks and intensities due to free aniline in the mass spectrum of **5b** (70 eV, 90 °C) compared with literature values[25] (m/e, I_{obsd}, $I_{lit.}$): 93, 100, 100; 66, 26, 33; 65, 15, 18; 39, 9, 18; 92, 11, 11; 46.5, 5, 9; 28, –, 8; 38, 3, 8.
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Extensive Configuration Interaction Studies of the Methylene Singlet–Triplet Separation

Sir:

For more than a decade now there have been two sets of conflicting experimental values for the $^3B_1 - {}^1A_1$ energy separation in CH_2, the simplest carbene; the "low" values[1] cluster about ~1–2 kcal/mol and the "high" values[2,3] near 8–9 kcal/mol. As if this situation were not confusing enough, a third experimental value, 19.5 ± 0.7 kcal, has recently been reported by Lineberger and co-workers[4] on the basis of their laser photodetachment study. This latest experimental value appears the most reliable, since the energy difference ΔE is obtained from a direct spectroscopic measurement.

Every ab initio theoretical study to date[5–7] has rejected the 1–2-kcal ΔE value, and all but one[8] have yielded singlet–triplet separations even larger than the old "high" value of 8–9 kcal. Among the most reliable theoretical treatments is that of Bender and co-workers,[9] whose configuration interaction (CI) calculations gave a ΔE value of 14.0 kcal. Since it appeared at the time (5 years ago) that additional refinements (e.g., basis set improvements) would lower the singlet–triplet separation, they estimated that the true ΔE value lies 1–5 kcal below the calculated 14.0 kcal. Thus, the lowest possible estimate nearly coincided with the "high" experimental value of 8–9 kcal. However, if Lineberger's experimental result[4] is the true ΔE value, this line of reasoning is incorrect and the calculated 14.0 kcal must be *increased* by ~5 kcal. In an attempt to clarify this point, it was decided to carry out state-of-the-art ab initio CI calculations. A communication by Roos[10] tackles the same problem using different theoretical methods.

Our present study begins with a "standard" set of calculations. Additional basis set and correlation effects will be evaluated relative to this standard. The standard basis was of the contracted gaussian variety,[11] labeled C(10s 6p 2d/6s 4p 2d), H(5s 1p/3s 1p). This basis is considerably larger than any to date[5–9] for which electron correlation has been variationally evaluated. This standard basis also reproduces to within 0.1 kcal the Hartree–Fock limit ΔE value[12] of 24.8 kcal/mol. Polarization function orbital exponents were optimized in the CI calculations and have the values 1.07, 0.33 (carbon d functions) and 0.95 (hydrogen p functions) for $^3B_1$ CH_2 and 1.05, 0.30 (carbon d functions) and 0.89 (hydrogen p functions) for $^1A_1$ CH_2.

The standard CI include all Slater determinants differing by one or two spin orbitals from the self-consistent field (SCF) reference configurations

$$^3B_1 \qquad 1a_1^2\ 2a_1^2\ 1b_2^2\ 3a_1\alpha\ 1b_1\alpha \tag{1}$$

$$^1A_1 \qquad 1a_1^2\ 2a_1^2\ 1b_2^2\ 3a_1^2 \tag{2}$$

Core and core-valence correlation effects were excluded by doubly occupying the $1a_1$ orbital in all determinants. This yields 4542 determinants for the $^3B_1$ state and 5359 determinants for the $^1A_1$ state when the standard 42 function basis set is employed. The CI calculations were performed on the Harris Slash Four minicomputer[13] using the BERKELEY system[14] of programs. Per point on the respective potential energy surfaces, roughly 57 and 66 min of elapsed time was required. Since the cost of time on the Harris Slash Four is only $8/hour, these computations were quite economical.

The equilibrium geometries of triplet (θ = 134°, r = 1.08 Å) and singlet (θ = 102.4°, r = 1.11 Å) methylene are well known[15,16] and were assumed here. The standard CI total energies were −39.06216 and −39.04065 hartrees, yielding a prediction of 13.5 kcal for ΔE ($^3B_1 - {}^1A_1$). The present variational $^3B_1$ total energy lies 31.4 kcal below the comparable result of Bender[9].

Following the "standard" calculations, a number of addi-