bonds in I may reflect a weakening of the Mo–S_t π bonds and a higher electron density at the terminal sulfur atoms.[9]

The contention that the reduction is not centered on the iron atom in I is strongly supported by the Mössbauer data. Preliminary results of the Mössbauer spectrum of I, in liquid N_2, show an isomer shift (IS) of 0.38 (3) mm/s vs. Fe and a quadrupole splitting of 1.04 (3) mm/s.[20] The low value of the IS in I indicates that the formal d orbital occupancy of the Fe center is smaller than that expected for either a 1+ or even a 2+ oxidation state. The cyclic voltammogram of I[21] shows a quasi-reversible reduction at ~−1.8 V and an *irreversible* oxidation at ~−0.10 V. Essentially the same results were reported previously by McDonald and co-workers.[16] The irreversibility of the oxidation wave clearly shows the instability and perhaps raises doubts as to the actual existence of a discreet $[(MoS_4)_2Fe]^{2-}$ complex anion.

A comment should be made concerning the recently reported $[Fe_4Mo_4S_{20}]^{6-}$ cluster.[22] The published electronic spectrum of this compound appeared to us similar, if not identical, to that of I (Figure 2). We repeated the synthesis of the "$[Fe_4Mo_4S_{20}]^{6-}$" anion as described in the literature. The Et_4N^+ salt of the product we obtained was found X-ray isomorphous to the corresponding derivative of I. Furthermore, the energies and absolute intensities of the electronic absorptions of the two compounds were virtually identical. On the basis of these results and similarities in the infrared and Mössbauer spectra between the two compounds, we propose that the "$[Fe_4Mo_4S_{20}]^{6-}$" anion is in fact the $[Fe(MoS_4)_2]^{3-}$ complex anion.

In conclusion, the facility of the Fe–MoS_4 chromophore to accept electrons makes this moiety ideally suited for the storage of electrons or perhaps even the relay of electrons under appropriate conditions. The reactivity of I is presently under study.

Acknowledgment. This work has been generously supported by grants from the National Science Foundation (CHE-79-0389) and the National Institutes of Health (GM-26671-01). The computing expenses have been covered by grants from The University of Iowa Graduate College.

Supplementary Material Available: Tables of atomic positional and thermal parameters and a list of observed and calculated structure amplitudes (14 pages). Ordering information is given on any current masthead page.

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Exceptional Micellar Stereoselectivity in Esterolysis Reactions: The Micelle–Enzyme Analogy

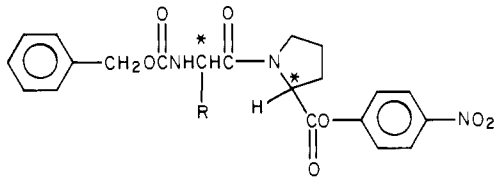
Sir:

The kinetic analogy between micelle- and enzyme-catalyzed reactions is well-known and extensively documented, particularly for esterolyses.[1] Impressive micellar rate enhancements attend the cleavage of activated esters by, e.g., imidazole- or thiol-functionalized surfactants.[2-4] However, progress has been less rapid in micellar control of esterolysis sterochemistry. Only modest enantioselectivity (~11%) was reported for cleavage of the enantiomeric *p*-nitrophenyl α-methoxyphenylacetates with *l-N-n*-dodecyl-*N*-methylephedrinium bromide micelles;[5] similar experiments with other chiral ammonium[6] or sulfoxonium[7] salts were unsuccessful.

The situation is somewhat better with various enantiomeric *N*-protected *p*-nitrophenyl amino acid ester substrates: enantioselectivities up to ~3:1 have been observed in esterolyses catalyzed by chiral histidine-functionalized surfactant micelles,[8] or by N^{α}-acylhistidines[9a] or L-alanyllaurylamide[9b] solubilized in, e.g., cetyltrimethylammonium (CTA) micelles. Even here, however, mechanistic details remain unclear, and related experiments with histidine or cysteine surfactants afforded insignificant enantioselectivity.[10] Not surprisingly, recent reviews of micellar catalysis have criticized the micelle–enzyme analogy, particularly citing the lack of substantial, predictable stereochemical control.[11,12]

In view of the currently modest experimental success,[5-10] and the pessimistic overall assessment,[11,12] we think it appropriate to disclose exceptional micellar stereoselectivity in the cleavage of diastereomeric dipeptide *p*-nitrophenyl (PNP) esters.[13] Our best cases are an order of magnitude greater than previous examples of micellar esterolytic stereoselectivity. Moreover, the new results can be fitted to a rational, predictive model.

Substrates I–V were generally synthesized by mixed anhydride coupling of the appropriate D- or L-benzyloxycarbonyl *Z*-protected amino acid to L-proline PNP ester in cold CH_2Cl_2 or THF.[14] The



I, R = CH_3 [(*Z*)-Ala-Pro-PNP]
II, R = $CH_2C_6H_5$ [(*Z*)-Phe-Pro-PNP]
III, R = CH_2-(3-indolyl) [(*Z*)-Trp-Pro-PNP]
IV, R = $CH_2CH(CH_3)_2$ [(*Z*)-Leu-Pro-PNP]
V, R = $CH(CH_3)_2$ [(*Z*)-Val-Pro-PNP]

n-$C_{16}H_{33}\overset{+}{N}(CH_3)_2CH_2CH_2SH,Cl^-$

VI (16-SH)

products were purified by crystallization and/or chromatography

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(13) We previously reported kinetic stereoselectivities of 3.9–4.3 in micellar esterolysis of (*Z*)-(L- or D-)Ala-L-Pro-PNP by thiol-functionalized surfactants: Moss, R. A.; Lee, Y-S.; Lukas, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 2499.
(14) (a) Substrates IV were prepared by DCC/HOBt coupling of (*Z*)-Leu to Pro-OMe. Controlled hydrolysis then gave (*Z*)-Leu-Pro-OH, which was coupled to *p*-nitrophenol with DCC. For procedures, see: McDermott, J. R.; Benoiton, N. L. *Can. J. Chem.* **1973**, *51*, 2559. Bodanszky, M.; Du Vigneaud, V. *J. Am. Chem. Soc.* **1959**, *81*, 5688. (b) Details will appear in a full paper, and in the Ph.D. Dissertation of Y-S. Lee

0002-7863/80/1502-6646$01.00/0

Table I. Micellar Cleavage of Diastereomeric Proline-PNP Esters[a]

substrate	surfactant	k_ψ^{LL}, s^{-1}	k_ψ^{DL}, s^{-1}	k_ψ^{LL}/k_ψ^{DL}	$\frac{(k_\psi^{LL}/k_\psi^{DL})_{16\text{-SH}}}{(k_\psi^{LL}/k_\psi^{DL})_{CTACl}}$	$\frac{(k_\psi^{LL})_{16\text{-SH}}}{(k_\psi^{LL})_{CTACl}}$
(I) (*Z*)-Ala-Pro-PNP	buffer	0.00044	0.00083	0.53		
	CTACl	0.00625	0.0104	0.60		
	16-SH	9.42	2.18	4.3	7.2	1500
(II) (*Z*)-Phe-Pro-PNP	buffer[b]	0.00010	0.00028	0.36		
	CTACl	0.00225	0.0065	0.35		
	16-SH	14.5	7.30	2.0	5.7	6400
(III) (*Z*)-Trp-Pro-PNP	buffer[b]	0.00009	0.00031	0.3		
	CTACl	0.00117	0.00412	0.28		
	16-SH	24.4	4.85	5.0	18	21000
(IV) (*Z*)-Leu-Pro-PNP	buffer[c]	0.00012	0.00035	0.34		
	CTACl	0.00145	0.0089	0.16		
	16-SH	14.8	5.82	2.5	16	10000
(V) (*Z*)-Val-Pro-PNP	buffer	0.000040	0.00028	0.14		
	CTACl	0.00076	0.0074	0.10		
	16-SH	10.6	3.27	3.2	32	14000

[a] See text for structures, reaction conditions, and abbreviations. [b] These values are extrapolated to pure buffer from four dioxane–buffer runs over a range of 10–30% dioxane. Although substrates II or III were not completely soluble in pure buffer at 2×10^{-5} M, such concentrations were easily obtained in 4×10^{-3} M surfactant solutions (absence of a Tyndall effect). [c] LL-IV required the addition of 2.5% dioxane for complete solubilization in buffer.

on Sephadex LH-20. Each diastereomer was characterized by a satisfactory elemental analysis, homogeneous TLC behavior, and a structurally consistent NMR spectrum.[14b]

Kinetic studies were performed in 0.02 M phosphate buffer [pH 8.0, μ = 0.05 (KCl)] usually containing 0.5–1 vol % dioxane. Pseudo-first-order rate constants were evaluated by monitoring the release of *p*-nitrophenoxide ion at 400 nm, and substrate and surfactant concentrations were fixed at 2.0×10^{-5} and 4.0×10^{-3} M, respectively. Least-squares rate constants ($r > 0.999$) appear in Table I, represent mean values of two or more runs, and were reproducible to <4% average deviation from the mean. Micellar cleavages of I–III were examined with a full range of functional surfactants, including 16-Im and AS-Cys.[14b,15] However, the greatest stereoselectivities were obtained with 16-SH (VI). Accordingly, Table I deals with three cleavage conditions: buffer alone, micellar CTACl, and micellar 16-SH.

Consideration of Table I yields the following observations. (a) In buffer alone, the D,L substrates cleave more rapidly than their L,L isomers. (b) Solubilization in micellar CTACl results in modest rate enhancements (factors of ~10–20) but, excepting IV, does not alter stereoselectivity; i.e., catalysis is generally comparable for diasteromeric substrates. (c) Solubilization in 16-SH affords very large rate enhancements, relative to CTACl, and pronounced stereoselectivity for cleavage of the L,L substrates. Indeed, comparing the L,L selectivities expressed in micellar 16-SH with the D,L preferences exhibited in micellar CTACl [$(k_\psi^{LL}/k_\psi^{DL})_{16\text{-SH}}/(k_\psi^{LL}/k_\psi^{DL})_{CTACl}$], we observe net stereoselectivities of 32 (Val-Pro, V), 18 (Trp-Tro, III), and 16 (Leu-Pro, IV). These are an order of magnitude larger than previously observed micellar stereoselectivities.[5-10] Note, also, that the largest micellar rate enhancements are observed with these same substrates: $(k^{LL})_{16\text{-SH}}/(k^{LL})_{CTACl}$ ratios are 21 000, 14 000, and 10 000 for III, V, and IV.

These exceptional stereoselectivities can be rationalized with reference to *specific* substrate–surfactant interactions *within* the substrate–micelle complex. CPK molecular models of the L,L substrates I–V, when arranged in extended peptide conformations, possess "clefts" defined by their Pro and PNP moieties, and by the R groups of their variable amino acids. The CH_2 chain of 16-SH neatly fits into these clefts, poising the $-CH_2CH_2S^-$ functionality slightly above and to the rear of the substrates' scissile carbonyl carbons. The models thus suggest that when L,L-I–V are optimally arranged for hydrophobic bonding to 16-SH the latter's thiolate moiety is optimally positioned for attack. Moreover, this arrangement "buries" the substrates' hydrophobic *Z* groups in the micellar interior, while their scissile carbonyl oxygens and PNP aromatic rings are proximal to the surfactant's quaternary nitrogen, where favorable electrostatic interactions should exist. In support of this model, notice that $(k_\psi^{LL})_{16\text{-SH}}$ or $(k_\psi^{LL})_{16\text{-SH}}/(k_\psi^{LL})_{CTACl}$ generally increase as the R groups of L,L-I–V become larger and more hydrophobic, i.e., as they increasingly "reinforce" the "walls" of the L,L-substrates' clefts.[16]

In contrast, extended conformers of D,L-I–V possess poorer binding sites for 16-SH because their R groups project *away* from the hydrophobic "faces" or clefts of the dipeptides. In terms of aggregate micellar hydrophobic interactions, D,L substrates may bind as strongly as L,L substrates to CTACl or 16-SH micelles,[17] but such binding should not orient the D,L substrates for optimal thiolate–carbonyl interaction, and their cleavages by 16-SH are less facile than those of their L,L isomers.[18]

Despite the "looseness" of micelle–substrate complexes,[12] micelle-mediated reactions are here shown to achieve substantial stereoselectivities. What appears to be crucial is that certain "oriented" micelle–substrate complexes, among the myriad of potentially available ones, are preferred *and* productive. Indeed, it is now recognized that enzymes need not tightly bind their substrates (which would only stabilize the enzyme–substrate complex or ground state); rather, enzymatic effectiveness depends on tight binding of the *transition state*, following upon weak binding of the substrate.[20] Refinement and extension of the present results and models are in progress.

Acknowledgment. We thank the National Science Foundation and the National Cancer Institute for financial support. The

(15) See ref 13 for the structures of these imidazole and cysteine functional surfactants.

(16) L,L-I–V can similarly interact with CTACl, but an analogous arrangement is no longer productive because CTACl is not functionalized. Accordingly, $(k_\psi^{LL})_{CTACl}$ or $(k_\psi^{LL})_{CTACl}/(k_\psi^{LL})_{buffer}$ show no particular dependence on substrate hydrophobicity in contrast to $(k_\psi^{LL})_{16\text{-SH}}$ or $(k_\psi^{LL})_{16\text{-SH}}/(k_\psi^{LL})_{CTACl}$; see Table I.

(17) Analyses[1b] of k_ψ vs. [surfactant] profiles for D,L-I or L,L-I with micellar AS-Cys[4] yield similar values of K/N (binding constant/aggregation number).[14b]

(18) The scissile carbonyl groups of D,L-I–V appear more accessible to solvent than those of L,L-I–V. This might permit more effective hydration of the developing C–O^- during OH^- attack, and could explain the more rapid cleavage of the D,L substrates in buffer or CTACl. Alternatively, it is possible that, under the latter conditions, I–V cleave partially (or entirely) by base-catalyzed intramolecular displacement on the Pro ester carbonyl by the nitrogen of the adjacent amino acid residue.[19] Were this the case, the 16-SH/CTACl stereoselectivity ratios in Table I would reflect a change of mechanism from intramolecular-assisted cleavage in buffer (D,L selective) to micellar-SH cleavage in 16-SH (L,L selective for reasons discussed above). The mechanism of nonmicellar hydrolysis of the dipeptides is under investigation.

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stopped-flow spectrometer was purchased under P.H.S. Grant RR-7058-09 to Rutgers University. We thank Professor U. Tonellato (Università di Padova, Italy) for useful discussions. R.A.M. is grateful to NATO (Grant 1619) for travel support to the Università di Padova.

(21) Colgate-Palmolive Fellow, 1979-1980.

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Metal Clusters with Exposed and Low-Coordinate Nitride Nitrogen Atoms

Sir:

In pursuing possible analogies between metal surfaces and metal clusters,[1] we have sought nitride clusters with exposed and possibly reactive nitrogen atoms to allow experimental comparisons between ammonia synthesis on metal surfaces and the possible stoichiometric or catalytic hydrogenation of nitrogen with metal clusters. To date, only two nitride clusters have been reported,[2] namely, the isostructural and trigonal-prismatic $[Co_6N(CO)_{15}^-]$ and $[Rh_6N(CO)_{15}^-]$, both of which contained interstitial rather than exposed nitride nitrogen atoms. We describe here the synthesis and structural characterization of a prototypic series of iron nitride clusters in which the nitrogen atoms are exposed and of low coordination number, namely, four and five. The term nitride is used to denote species in which a nitrogen atom is only within bonding distance of metal atoms.

An extension of our synthetic methods for low-coordinate carbide clusters[3] was successfully modified for the analogous nitrides. The Fe_4N cluster anion $[Fe_4N(CO)_{12}^-]$ (**1**) was prepared by the reaction of $NOBF_4$ with $Na_2Fe_2(CO)_8$ in the presence of excess iron pentacarbonyl (diglyme solution at 130 °C).[4] This anionic nitride was protonated by strong acids in toluene solution to form the neutral nitride $HFe_4N(CO)_{12}$ (**2**).[5] In these solutions, excess acid, e.g., CF_3SO_3H, did not yield the cation $[HFe_4NH(CO)_{12}^+]$.

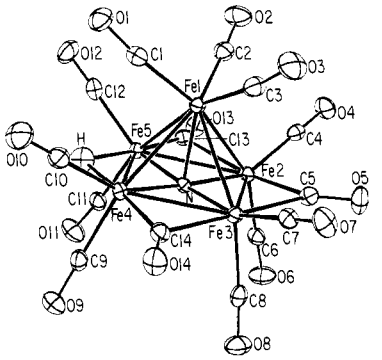

Figure 1. Atom labeling scheme for $HFe_5N(CO)_{14}$.

It is important to note that the synthesis of $[Fe_4N(CO)_{12}^-]$ is very temperature sensitive; below 130 °C, a nitrosyl complex was formed, and above, an Fe_5N cluster was the major product. When the synthesis mixture of $NOBF_4$, $Na_2Fe_2(CO)_8$, and $Fe(CO)_5$ was heated for either prolonged periods or at temperatures above 130 °C, the cluster $[Fe_5N(CO)_{14}^-]$ (**3**) was formed.[6] This anion was converted to $HFe_5N(CO)_{14}$ (**4**) on dissolution in a sulfuric acid–toluene mixture.[7] A third derivative in this Fe_5N system, $[HFe_5N(CO)_{13}^{2-}]$ (**5**), was obtained from **3** by reaction with $LiB(C_2H_5)_3H$.[8]

By analogy to the iron carbide structures[3,9] and from the general molecular orbital calculations of Lauher,[10a] our 62-electron four-iron nitrides should have butterfly structures, and our 74-electron five-iron nitrides should have square-pyramidal structures. Spectroscopic data for the Fe_4N complexes **1** and **2**, in comparison with those of the precise carbide analogues $[HFe_4C(CO)_{12}^-]$ and $[Fe_4C(CO)_{12}^{2-}]$,[3,10b] strongly implicate an Fe_4 butterfly with the nitride nitrogen atom centered above the wings. Infrared studies established that for **2** all CO ligands were terminal (as in the carbides), and the hydride ^1H NMR resonance at 40.2 ppm was in a characteristic range for such iron hydride clusters.[3] The carbonyl ^{13}C NMR spectrum for **2** consisted of a sharp singlet and two very broad resonances at 25 °C and a set of four resonances of 4:4:2:2 intensity ratios at −80 °C.[11] These resonances can be assigned to the four CO environments of **2** as shown in A. An X-ray crystallographic analysis of $HFe_4N(CO)_{12}$ established the proposed butterfly structure with a 4-coordinate nitride atom.[12a] Average iron–iron distances were 2.62 (1) (apical–basal)

(1) E. L. Muetterties, T. N. Rhodin, E. Band, C. F. Brucker, and W. R. Pretzer, *Chem. Rev.*, **79**, 91 (1979).

(2) S. Martinengo, G. Ciani, A. Sironi, B. T. Heaton, and J. Mason, *J. Am. Chem. Soc.*, **101**, 7095 (1979).

(3) M. Tachikawa and E. L. Muetterties, *J. Am. Chem. Soc.*, **102**, 4541 (1980).

(4) The tetraethylammonium salt of **1** was prepared by reaction of $Na_2Fe(CO)_4 \cdot {}^3/_2C_4H_8O_2$ (4.5 g) with $Fe(CO)_5$ (9 mL) to which was added 60 mL of diglyme. After formation of $Na_2Fe_2(CO)_8$, $NOBF_4$ (1.5 g) was slowly added. The solution was heated to 130 °C for 1 h and then cooled. A black precipitate, which formed after addition of hexane, was triply washed with water. $(C_2H_5)_4NCl \cdot H_2O$ (2.0 g) was added to the precipitate, and the product, $[(C_2H_5)_4N][Fe_4N(CO)_{12}]$, was extracted with dichloromethane. An equal volume of ethanol was added to the extract, and the volume of the resulting solution was reduced to $^1/_2$ under vacuum. After the solution was cooled to −25 °C, black crystals of $[(C_2H_5)_4N][Fe_4N(CO)_{12}]$ (300 mg, 3.3%) were formed: IR [ν(CO)/tetrahydrofuran] 2063 (vw), 2015 (s), 1990 (vs), 1967 (m), 1933 (w) cm^{-1}; ^{13}C NMR (dichloromethane, 0 °C) 215.6 (s, 6 CO), 218.2 (s, 6 CO) ppm. Anal. Calcd: C, 34.13; H, 2.86; N, 3.98. Found: C, 34.22; H, 3.09; N, 3.86.

(5) The tetraethylammonium salt $[(C_2H_5)_4N][Fe_4N(CO)_{12}]$ (200 mg) was added to a Schlenk flask containing 50 mL of toluene and 2 mL of H_2SO_4, and the two-layer system was stirred rapidly. The red-brown toluene layer was collected through Celite, and the toluene was removed under vacuum. The $HFe_4N(CO)_{12}$ product was recrystallized from CH_2Cl_2 at −30 °C: IR [ν-(CO)/hexane] 2053 (s), 2035 (m), 2023 (m), 2015 (vw), 1994 (w) cm^{-1}; mass spectrum, 575 (p^+) followed by successive loss of 12 CO, 183 $(HFe_3N)^+$; ^{13}C NMR (tetrahydrofuran, −88 °C) 215.1 (s, 2 CO), 214.7 (d, J = 8.7 Hz, 4 CO), 211.2 (s, 4 CO), 206.1 (s, 2 CO) ppm. Anal. Calcd: C, 25.08; H, 0.18; N, 2.44. Found: C, 25.09; H, 0.26; N, 2.44.

(6) $[(C_2H_5)_4N][Fe_5N(CO)_{14}]$ was prepared analogously to **1** except that the reaction temperature was increased to 145 °C and reaction time to 2 h (yield, 66% based on $NOBF_4$): IR [ν(CO)/CH_2Cl_2] 2062 (w), 2001 (vs, br), 199] (vs, br), 1970 (m, sh), 1805 (w, br) cm^{-1}; ^{13}C NMR (dichloromethane, 0 °C) 221.4 (s, 11 CO), 215.9 (s, 3 CO) ppm. Anal. Calcd: C, 32.39; H, 2.47; N, 3.43. Found: C, 32.47; H, 2.56; N, 3.40.

(7) $HFe_5N(CO)_{14}$ prepared in the same manner as **2** had the following spectra: mass spectrum, 687 (p^+) followed by ions corresponding to loss of carbon monoxide molecules; IR [ν(CO)/hexane] 2053 (vs), 2034 (s), 2012 (w), 1981 (vw, br), 1871 (vw) cm^{-1}.

(8) To a tetrahydrofuran solution of $[(C_2H_5)_4N][Fe_5N(CO)_{14}]$ (**4**) (900 mg in 30 mL) was added 3.0 mL of 1 M $LiBEt_3H$ in tetrahydrofuran at −78 °C. After being warmed to ambient temperature, the solvent was removed under reduced pressure. $(C_2H_5)_4NCl \cdot H_2O$ (205 mg) was added to the resultant solid, and $[(C_2H_5)_4N]_2[HFe_5N(CO)_{13}]$ was obtained from methanol as deep brown plates (440 mg, 44%): IR [ν(CO)/CH_3CN] 1958 (vs), 1947 (s), 1912 (s), 1776 (w) cm^{-1}; ^1H NMR (CD_3CN) 3.11 (methylene), 1.15 (methyl), −12.28 (hydride at −40 °C) ppm. ^{13}C NMR (tetrahydrofuran, −80 °C) 213.5 (d, 2 CO), 221.6 (s, 3 CO), 223.0 (d, 2 CO), 232.5 (br, s, 6 CO) ppm. Anal. Calcd: C, 37.90; H, 4.50; N, 4.57. Found: C, 37.72; H, 4.51; N, 4.60.

(9) E. H. Braye, L. F. Dahl, W. Hübel, and D. L. Wampler, *J. Am. Chem. Soc.*, **84**, 4633 (1962).

(10) (a) J. W. Lauher, *J. Am. Chem. Soc.*, **100**, 5305 (1978). (b) The cluster $HFe_4(\eta^2\text{-}CH)(CO)_{12}$ was shown by X-ray studies to have an Fe_4C butterfly geometry with the carbon atom above the wings. M. A. Beno, J. M. Williams, M. Tachikawa, and E. L. Muetterties, *ibid.*, **102**, 4542 (1980).

(11) The CO ^{13}C resonance for **1** consisted of two singlets from +20 to −80 °C. Facile CO site exchange had been observed[3] for the $[Fe_4C(CO)_{12}^{2-}]$ analogue.

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