around the platinum atom, the deviations from planarity being <0.01 Å. The enamine is bound to platinum through the olefinic C═C double bond, the midpoint of the C═C bond being ~0.20 Å displaced from the principal coordination plane. The double bond has a cis configuration and is nearly orthogonal to the coordination plane. The nonhydrogen atoms of the moiety CH—CH═CH—NH—C lie almost in a plane (deviations from planarity are <0.04 Å). The phenyl group forms an angle of ~10° with this plane, which is tilted of ~20° with respect to the normal from Pt to the double bond. Some relevant bond lengths follow: C(arom)—N = 1.39 (2), C(olef)—N = 1.37(2), C═C = 1.38 (2) Å; the bond angle C-N-C is 124.4 (5)°. The relatively short distance C(olef)—N [cf. N—Me = 1.48 (4) Å in 4-nitro-*N*,*N*-dimethylaniline[9]] is consistent with a substantial amount of conjugation of the nitrogen atom with the carbon-carbon double bond,[10] as well as with the aromatic ring. The Pt—C bond lengths are among the largest observed for monoolefin complexes[11,12] and are significantly different from each other (2.213 ± 0.014 and 2.314 ± 0.016 Å; see Figure 1). A comparable difference has been found in other Pt(II) complexes of olefinic compounds containing electron-releasing substituents, i.e., a *p*-(*N*,*N*-dimethylamino)styrene,[13] a vinyl alcohol,[12] and two vinyl ether complexes,[14] and is also consistent with the negative polarization of the C(2) atom arising from the quoted conjugation.[12,15]

We have observed the quoted isomerization β-ammonioalkenyl η^1 complex → η^2-enamine complex for a variety of primary aromatic amine derivatives; however, we have found a strong dependence of the isomerization rate on the basicity of the amine, a poorer basicity favoring the rearrangement reaction. As two limiting cases, the rearrangement was not observed for the *p*-anisidine ($pK_a = 5.34$[16]) derivative, whereas for the *p*-nitroaniline ($pK_a = 1.0$[16]) derivative only the η^2-enamine complex was isolable. Moreover, by using N-deuterated 2-chloroaniline the enamine complex specifically deuterated at the isopropyl secondary carbon atom was obtained. These findings suggest that the rearrangement very likely proceeds through the attack of an acidic N-H hydrogen of the zwitterionic complex (**1**) on the C(3) carbon atom with successive proton transfer from the C(1) atom to the C(2) atom and reconstitution of the double bond between the C(1) and C(2) atoms. It should be noted that the stereospecificity of this reaction leading to a coordinated cis olefin is also consistent with the proposed intramolecular mechanism.

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Supplementary Material Available: Table of the atomic coordinates and thermal parameters for *cis*-dichloro-η^2-[(*Z*)-2-chloro-*N*-(3 - methylbut-1-enyl)benzenamine](triphenylphosphine)platinum(II) (1 page). Ordering information is given on any current masthead page.

References and Notes

(1) De Renzi; A.; Di Blasio, B.; Panunzi, A.; Pedone, C.; Vitagliano, A. *J. Chem. Soc., Dalton Trans.* **1978,** 1392.

(2) IR (Nujol mull), cm^{-1}: 3375 (m) (NH); 1590 (s), 1550 (s) (C═C—N), 317 (s), 284 (s) (Pt—Cl). The C═C stretching is shifted by the coordination at frequencies lower than usual.[6] The Pt—Cl stretching bands are shifted to higher frequencies relative to the starting zwitterionic complex (**1**),[1] this being consistent with the disappearance of the trans-weakening C—Pt σ bond. Cf.: Mann, B. E.; Shaw, B. L.: Tucker, N. I. *J. Chem. Soc. A* **1971,** 2667. Empsall, H. D.; Shaw, B. L.; Stringer, A. J. *J. Organomet. Chem.* **1975,** *96*, 461.

(3) $PtCl_2(PPh_3)(ClC_6H_4NHCH^a{=}CH^bCH^cMe_2)$, isomers A and B. ^1H NMR (270 MHz, $CDCl_3$), δ (ppm): $T = 298$ K, 0.86 (d, 3 H), 1.47 (d, 3 H), 2.82 (br, 1 H), 3.23 (br, 1 H), 5.82 (br, 0.5 H), 6.04 (br, 0.5 H), 6.9–8.4 (20 H); $T = 243$ K, for isomer A (excluding aromatic protons), 0.82 (d, Me), 1.47 (d, Me), 3.2 (m, H^c), 2.77 (ddd, H^b, $J_{H^b-H^c} = 10.5$, $J_{H^b-H^a} = 5.9$, $J_{H^b-P} = 3.5$ Hz), 5.99 (dd, H^a, $J_{H^a-H^b} = 5.9$, $J_{H^a-NH} = 13$ Hz); for isomer B (excluding aromatic protons), 0.86 (d, Me), 1.43 (d, Me), 2.86 (m, H^c), 3.21 (ddd, H^b, $J_{H^b-H^c} = 9.8$, $J_{H^b-H^a} = 12$, $J_{H^b-P} = 7$ Hz), 5.81 (d, NH, $J_{NH-H^a} = 12.5$ Hz), 7.65 (H^a, obscured by the aromatic proton signals, but revealed by double irradiation techniques). ^{13}C NMR (67.88 MHz, $CDCl_3$), δ (ppm) (excluding aromatic carbons): $T = 243$ K, 20.23 (Me), 22.72 (Me), 23.71 (Me), 25.23 (Me), 26.43 ($C^c{}_A$), 30.41 ($C^c{}_B$), 65.88 ($C^b{}_A$), 71.70 ($C^b{}_B$), 110.41 ($C^a{}_A$), 115.10 ($C^a{}_B$). In the ^1H NMR spectra the assignments were made with the aid of decoupling experiments and through selective deuteration of the NH and/or H^c protons. In the ^{13}C NMR spectra the assignments were made with the aid of selective ^1H-decoupling techniques. The ^{195}Pt satellite peaks of the olefinic protons were observable as broad bands ($J_{H^b{}_A-Pt} \simeq 70$, $J_{H^b{}_B-Pt} \simeq 55$, $J_{H^a{}_A-Pt} \simeq 55$ Hz). The satellite peaks of the olefinic carbons disappeared in the noise and were not detected.

(4) $ClC_6H_4NHCH^a{=}CH^bCH^cMe_2$. ^1H NMR (270 MHz, $CDCl_3$), δ (ppm): 1.07 (d, 2 Me), 2.60 (m, H^c), 4.49 (dd, H^b), 6.16 (d, br, NH), 6.27 (dd, H^a), 6.70 (dt, 1 H), 6.86 (dd, 1 H), 7.15 (dt, 1 H), 7.29 (dd, 1 H).

(5) This hypothesis appears to be the only consistent with the spectral and analytical data. In fact the compound was found to be monomeric and undissociated in solution by molecular weight determination [calcd 724, found (osmometry) 732], and the possibility of a π–σ rearrangement such as $[PtCl_2(PPh_3)\text{-}\eta^2\text{-}(ArNHCH{=}CHCHMe_2)] \rightleftharpoons [PtCl_2(PPh_3)\text{-}\eta^1(ArN^+H{=}CHC^-HCHMe_2)]$ (cf. Tsutsui, M.; Courtney, A. *Adv. Organomet. Chem.* **1977,** *16*, 241–252) can be ruled out on the basis of the ^{13}C chemical shifts of the two isomers (the conversion π-bonded sp^2 carbon → σ-bonded sp^3 carbon is expected to result in an upfield shift in the range 15–80 ppm; cf., e.g., Hughes, R. P.; Powell, J. *J. Organomet. Chem.* **1973,** *60*, 427). In addition the IR spectra of the compound in the solid state (single crystals in Nujol mull) and in solution ($CHCl_3$) are nearly identical, supporting the conclusion that only a conformational equilibrium is involved in solution.

(6) De Savignac, A.; Bon, M.; Lattes, A. *Bull. Soc. Chim. Fr.* **1972,** 3167.

(7) Ahlbrecht, H.; Blecher. J.; Hanisch, H.; Papke, G.; Reiner, T. *Tetrahedron* **1973,** *29*, 3079. De Jeso, B.; Pommier, J. C. *J. Organomet. Chem.* **1977,** *137*, 23.

(8) Crystals are orthorhombic, space group *Pbca*; $a = 21.199$ (10), $b = 17.550$ (10), $c = 15.567$ (7) Å; $V = 5791.6$ Å^3; $Z = 8$; d(calcd) = 1.66, d(exptl) = 1.64 g/cm^3. Intensities were collected on a Philips PW 1100 computer-controlled four-circle diffractometer (Mo Kα radiation) using the ϑ–2ϑ scan method. The positional and anisotropic thermal parameters of all atoms were refined by full-matrix least-squares calculations. The resulting discrepancy index is $R_F = 0.059$ for the 5097 reflections having $I \geq 3\sigma(I)$.

(9) Mak, T. C. W.; Trotter, J. *Acta Crystallogr.* **1965,** *18*, 68.

(10) Ahlbrecht, H.; Papke, J. *Tetrahedron Lett.* **1972, 4443.**

(11) References quoted by Bruce, M. I. *J. Organomet. Chem.* **1974,** *75*, 335; **1974,** *89*, 215; **1976,** *115*, 17; **1977,** *126*, 1; **1978,** *151*, 313; **1979,** *167*, 361.

(12) Cotton, F. A.; Francis, J. N.; Frenz, B. A.; Tsutsui, M. *J. Am. Chem. Soc.* **1973,** *95*, 2483.

(13) Nyburg, S. C.; Simpson, K.; Wong-Ng, W. *J. Chem. Soc., Dalton Trans.* **1976,** 1865.

(14) Sartori, F.; Leoni, L. *Acta Crystallogr., Sect. B* **1976,** *32*, 145. Elder, R. C.; Pesa, F. *Ibid.* **1978,** *34*, 268.

(15) Busse, P.; Pesa, F.; Orchin, M. *J. Organomet. Chem.* **1977,** *140*, 229.

(16) West, R. C., Ed. "Handbook of Chemistry and Physics", 56th ed.; CRC Press: Cleveland, Ohio, 1975; p D 147.

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$^2B_2$ Benzoyloxy, a Delocalized σ Radical

Sir:

In connection with other work we have needed to know the spin distribution in the ground state of benzoyloxy radical.[1] Theory alone is of little help. The "doublet-instability" problem, which afflicts calculations on the allyl radical even at the Hartree-Fock limit,[2] is compounded in heteroatom-containing analogues by alternative Σ and Π ground states.[3] Calculations including limited configuration interaction seem to avoid the former problem, but do not permit a clear choice of ground state, since they predict Σ–Π gaps of <10 kcal/mol for many heteroallylic radicals.[4] Calculation of formyloxy by STO 4-31G CI with geometry optimization predicts that the $^2A_2$ (Π) ground state of C_{2v} symmetry lies only 1.4 kcal/mol below the $^2A'$ (Σ) state of C_s symmetry.[4]

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Table I. Oxygen-17 Hyperfine Splittings of Benzoyloxy[a]

	label position					
	carbonyl			peroxy		
eigenvalues	17.1 (5)	19.9 (5)	78.9 (2)	7.5 (7)	10.6 (6)	67.7 (4)
eigenvectors						
a^*	0.0425	0.8505	0.5243	0.7631	0.1916	0.6173
b	0.9624	−0.1757	0.2071	0.5789	−0.6273	−0.5209
c	0.2683	0.4958	−0.8260	−0.2874	−0.7548	0.5896
angular error, deg[b]	2.2	2.2	0.2	16	16	0.8
a_{iso}, 3B	38.6, 60.4			28.4, 58.8		
% s, % p[c]						
ref 11a	0.82, 41.9			0.61, 40.9		
ref 11b	0.73, 35.9			0.54, 35.0		
no. obsd. rms dev[d]	83, 1.7			104, 1.9		

[a] Splitting constants (gauss) are twice the value measured for the radical pair.[1] Estimated standard deviation in the last digit is given parenthetically. [b] See ref 16. [c] Oxygen s-orbital and p-orbital spin densities inferred using the indicated sources for proportionality constants. [d] Number of orientations in which $m_O = \pm 5/2$ transitions were measured, and the root mean square deviation of observed hfs from theory after a least-squares fit with weighting for experimental uncertainties in line position and mounting angle.

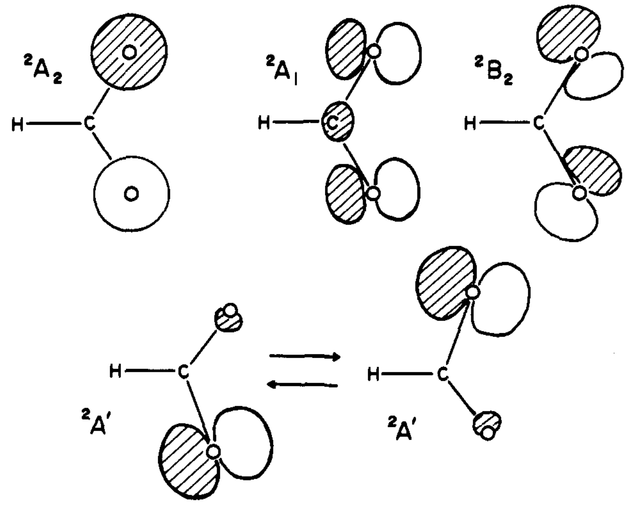

Figure 1. Lowest vacant INDO orbital for several electronic configurations of C_{2v} (top row) and C_s formyloxy radical. σ orbitals are outlined at 0.15 au in the molecular plane. π orbital of $^2A_2$ is outlined at 0.1 au at 0.3 Å above the plane. No single MO portrays the net spin distribution in a spin-unrestricted calculation, but in this case the β LUMO gives the best picture of excess α spin density.

Numerous less sophisticated semiempirical and ab initio calculations on formyloxy, acetoxy, and benzoyloxy have given various predictions of ground-state electronic configuration and geometry.[1a,5] There is, however, virtual unanimity on two points: (1) that the substituent on the carbonyl carbon should exert little influence on the spin distribution and energy, and (2) that the lowest Σ state should distort from C_{2v} to C_s symmetry to allow mixing of the $^2A_1$ and $^2B_2$ states to give a $^2A'$ state. The LUMOs which account for most of the spin in INDO spin-unrestricted calculations of these various states are shown in Figure 1.[1a] A $^2A'$ ground state could be associated with the type of double-minimum potential that has complicated studies of many other species.[6]

EPR spectra have been reported for acyloxy radicals with saturated,[7] vinylic,[8] propargylic,[9] and aromatic[1] substituents in ionic, hydrogen-bonded, and van der Waals crystals. Similarity among the g tensors of these species suggests that they possess a common ground state. Each shows a g eigenvector in the direction perpendicular to the OCO plane of the radical precursor which is shifted from 2.002 by 0.005 (±0.001), and each shows in-plane g shifts of 0.022 (±0.005) and 0.001 (±0.001). In most cases these g shifts, together with the anisotropy of distant proton hfs, have been used to argue for $^2A'$ ground state with 70–85% of the spin density on a single oxygen atom.[8-10] Because interpretation of g shifts depends heavily on completely speculative values for excitation energies, and because the proton hfs is weak, these arguments lack rigor.

We previously used two additional lines of evidence, CIDNP and absence of cylindrical symmetry in the fine-structure tensors for radical pairs, to infer a highly delocalized spin distribution for benzoyloxy.[1] These data were consistent with either the $^2B_2$ or the $^2A_2$ state. Since theory suggested that a highly delocalized Σ state was unlikely, we favored the $^2A_2$ ground state.

The oxygen hfs tensors of the benzoyloxy-perdeuteriomethyl radical pair prove that the ground state of benzoyloxy is $^2B_2$. Samples of acetyl benzoyl peroxide were prepared by autoxidizing benzaldehyde in acetic-d_6 anhydride, using in one case oxygen gas containing 76% ^{17}O and in the other benzaldehyde-^{17}O (40%, from hydrolysis of benzilidene bromide in quinoline with $H_2{}^{17}O$). Single crystals of both peroxy- and carbonyl-labeled peroxide were grown and studied at 7–25 K by previously described methods.[1a] Oxygen hfs was measured in the T_{-1}–T_0 transition, and fit by an Hamiltonian consisting of nuclear Zeeman and hyperfine terms with the assumption that the electron spin is quantized by the applied field. The results are presented in Table I.

The anisotropic hfs constants, which differ by <3%, imply that almost all of the spin is distributed equally between the two oxygens in 2p orbitals.[11] The isotropic hfs constants of the oxygens differ by 26%, but together they account for <1.5% of the spin. A single $^2A'$ radical is excluded, and the absence of site symmetry argues against equal populations for equilibrating $^2A'$ radicals. The $m_O = \pm 5/2$ transitions are not broadened at 5 K in a crystal orientation which gives them a 520-MHz splitting. Thus a potential-energy barrier between classically equilibrating $^2A'$ radicals would have to be significantly less than 100 cal/mol (35 cm^{-1}), which would certainly be below the lowest vibrational level.

The most unambiguous evidence in favor of the $^2B_2$ ground state is the relative orientation of the unique hfs eigenvectors, which should coincide with the symmetry axes of the spin-containing 2p orbitals of oxygen. Diagonalizing the INDO spin density matrix in the neighborhood of the oxygen atoms predicts that the angle between these vectors in the $^2A_2$, $^2A_1$, $^2B_2$, and equilibrating $^2A'$ states of benzoyloxy should be 0, 3, 118, and 26°, respectively. The LUMOs of Figure 1 show angles of 0, 18, 110, and 35°, respectively.

INDO predicts spin densities of 0.54 on each oxygen, −0.10 on the carbonyl carbon, and <0.01 on every other atom of $^2B_2$ benzoyloxy. Our hfs constants imply oxygen spin densities 23–35% smaller than this. We suspect that the discrepancy is due more to inadequacy of the published hfs-to-spin-density conversion factors than to failure of INDO or to thermal averaging of the hfs tensors.[12,13] The remote possibility that the

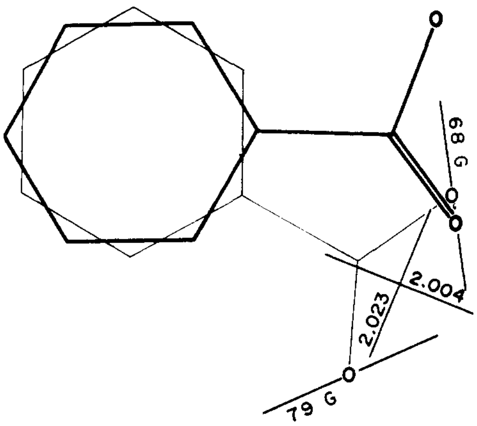

Figure 2. *g* and hfs eigenvectors of benzoyloxy projected on the plane of the original atomic locations in acetyl benzoyl peroxide (heavy lines). Implied radical position indicated by light lines.

isotopic oxygen might influence the spin distribution by perturbation of resonance[14] can be eliminated by the observation that fine-structure splittings in the methyl-benzoyloxy radical pair are identical for labeled and unlabeled material in the same crystal. This measurement would have been sensitive to a shift of 2% spin density between the two oxygens.

Figure 2 projects the unique hfs eigenvectors and the in-plane *g* eigenvectors onto the plane of the benzoyloxy atoms of undamaged acetyl benzoyl peroxide.[15] It is clear that, contrary to previous hypothesis,[10] the radical has undergone substantial in-plane rotation from its original position. The *g* tensor, which was previously used to argue for the $^2A'$ state,[10] is now seen to be in accord with the $^2B_2$ assignment. The vector product of the *g* eigenvectors of Figure 2 diverges from the normal to the original least-squares phenyl plane by 2°; that of the hfs eigenvectors diverges from the normal by 5.6°. Thus the tensors agree that the rotation is in plane and that the conformation of the radical is planar. They differ in assigning the amount of rotation: *g* implies 23° rotation, and hfs implies 30°. We believe this discrepancy is well beyond experimental error.[16]

Using the *g* shifts observed and matrix elements estimated from the INDO LUMOs of Figure 1, one can guess at the energy gaps between the $^2B_2$ ground state and the $^2A_2$ and $^2A_1$ excited states of benzoyloxy. The largest *g* shift predicts that the $^2A_2$ state lies 13 kcal/mol above $^2B_2$. The intermediate *g* shift implies that the $^2A_1$ state lies 55 kcal/mol above $^2B_2$. Even given that the two Σ states should have quite different OCO angles, the latter gap seems too high, especially since the radical is photodecarboxylated by light as red as 25 kcal/einstein.[5f]

The above observations should provide sensitive tests of the quality of wavefunctions for acyloxy radicals, as well as allowing interpretation of the arrangement of numerous radicals and radical pairs in single crystals.

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References and Notes

(1) (a) Karch, N. J.; Koh, E. T.; Whitsel, B. L.; McBride, J. M. *J. Am. Chem. Soc.* **1975,** *97,* 6729. (b) McBride, J. M.; Vary, M. W.; Whitsel, B. L. *ACS Symp. Ser.,* **1978,** No. 69, 208. (c) Vary, M. W.; McBride, J. M. *Mol. Cryst. Liq. Cryst.* **1979,** *52,* 133.

(2) Paldus, J.; Veillard, A. *Chem. Phys. Lett.* **1977,** *50,* 6.

(3) For some references see: (a) Evleth, E. M.; Horowitz, P. M.; Lee, T. S. *J. Am. Chem. Soc.* **1973,** *95,* 7948. (b) Koenig, T.; et al. *Ibid.* **1974,** *96,* 4573.

(4) Baird N. C.; Taylor, K. F., personal communication from Professor Baird.

(5) (a) Koenig, T.; Wielesek, R. A.; Huntington, J. G. *Tetrahedron Lett.* **1974,** 2283. (b) Kikuchi, O. *Ibid.* **1977,** 2421. (c) Kikuchi, O.; Utsumi, K.; Suzuki, K. *Bull. Chem. Soc. Jpn.* **1977,** *50,* 1339. (d) Kikuchi, O.; Hiyama, A.; Yoshida, H.; Suzuki, K. *Ibid.* **1978,** *51,* 11. (e) Newton, M. D., personal communication. (f) Whitsel, B. L., Ph.D. Thesis, Yale University, 1977.

(6) For example: Brown, H. C. "The Nonclassical Ion Problem"; Plenum Press: New York, 1977. Griller, D.; Ingold, K. U.; Krusic, P. J.; Fischer, H. *J. Am. Chem. Soc.* **1978,** *100,* 6750, and references cited therein.

(7) (a) Box, H. C.; Freund, H. G.; Lilga, K. T.; Budzinsky, E. E. *J. Phys. Chem.* **1970,** *74,* 40. (b) Budzinsky, E. E.; Box, H. C. *J. Chem. Phys.* **1975,** *63,* 4927.

(8) (a) Iwasaki, M.; Eda, B.; Toriyama, K. *J. Am. Chem. Soc.* **1970,** *92,* 3211. (b) Eda, B.; Iwasaki, M. *J. Chem. Phys.* **1971,** *55,* 3442. (c) Minikata, K.; Iwasaki, M. *Ibid.* **1972,** *57,* 4758.

(9) Muto, H.; Toriyama, K.; Iwasaki, M. *J. Chem. Phys.* **1972,** *57,* 3016.

(10) Yim, M. B.; Kikuchi, O.; Wood, D. E. *J. Am. Chem. Soc.* **1978,** *100,* 1869.

(11) (a) Morton, J. R. *Chem. Rev.* **1964,** *64,* 453. (b) Morton, J. R.; Preston, K. F. *J. Magn. Reson.* **1978,** *30,* 577.

(12) Tabulated values of calculated atomic hfs couplings differ by 15% for oxygen.[11] Since the atomic wave functions may change substantially on incorporation into a molecule, an error of 25% or more for molecular applications is not surprising.

(13) The oxygen hfs does not vary significantly from 65 to 4 K.

(14) Saunders, M.; Kates, M. R. *J. Am. Chem. Soc.* **1977,** *99,* 8071.

(15) These eigenvectors lie within 3° of the phenyl plane before projection.

(16) Angular errors were estimated by a procedure developed by D. W. Walter of these laboratories. It involves rediagonalizing the diagonal tensor after replacing the zero off-diagonal elements by their standard deviations estimated during least-squares refinement of the tensor. The shift in eigenvector direction measures the angular error. The hfs angular errors are given in Table I; those of the *g* eigenvectors are 1.6, 3.9, and 3.8° for the large, intermediate, and small *g* shifts, respectively.

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Metal Clusters. 24.[1] Synthesis and Structure of Heteronuclear Metal Carbide Clusters

Sir:

Metal carbide clusters,[2] a well-established and potentially very large group of clusters, are of substantial chemical interest because the carbide carbon atom, if exposed or open to reagent attack, may have an extensive chemistry of some novelty. Also these clusters may provide, by formal analogy, information about carbon as a surface species and as an intermediate in catalytic CO hydrogenation reactions.[3] In the carbide clusters with exposed or peripheral carbide carbon atoms—e.g., $Fe_5C(CO)_{15}$ and its derivatives—we have found a low degree of reactivity[4] and therefore have sought heteronuclear analogues that might prove more reactive.[5] We describe here a general synthesis of heteronuclear metal carbide clusters for the cage[6] octahedral MM'_5C class and for the peripheral[6] square-pyramidal MM'_4C class as well as crystallographic confirmation of the proposed structures.

Octahedral $MFe_5C(CO)_xL_y{}^{z-}$ complexes were prepared by reaction of the anion $Fe_5C(CO)_{14}{}^{2-}$, derived from $Fe_5C(CO)_{15}$ and $Fe(CO)_4{}^{2-}$, with mono- or dinuclear transition-metal complexes that are either coordinately unsaturated or that have readily displaceable ligands (Scheme I).[7a] The heteronuclear $MFe_5C(CO)_xL_y{}^{z-}$ clusters have been isolated as tetraethylammonium salts which were characterized by elemental analysis.[7b] All of these compounds formed black crystals—solution-state colors were purple for the octahedral clusters and ranged from dark green to brown for the square-pyramidal clusters. These include clusters which are the first carbide clusters that contain metal atoms outside of the iron and cobalt groups.[2] Neutral octahedral clusters like $NiFe_5C(CO)_{16}$ showed a parent ion in the mass spectrometric experiment and all mass ions resulting from successive CO loss down to the $NiFe_5C$ ion; this neutral cluster was prepared by oxidation of the anionic $NiFe_5C(CO)_{15}{}^{2-}$ species.