(3) The largest scale dimerization reaction which we have done gave 1258 mol of dimer/mol of catalyst. Purple $Ta(\eta^5\text{-}C_5Me_5)Cl_2$(1-octene) (115 mg, 0.26 mmol) was added to 77.7 g (0.692 mol) of dry, O_2-free 1-octene to give a light orange color characteristic of a metallacyclopentane complex. After the mixture was heated at 100 °C for 20 h, the color was dark orange. GLC analysis showed that >97% of the product consisted of two dimers (see text). (A separate experiment showed that these initial products isomerize slowly after all of the monomer is consumed.) The mixture was passed through a short column of alumina to remove tantalum and vacuum distilled to give a 97% isolated yield of the dimer mixture.

(4) A typical dimerization reaction is done in 3 mL of toluene employing 0.2 mmol of any $Ta(\eta^5\text{-}C_5Me_5)Cl_2$(olefin) complex (usually the olefin is cyclooctene;[2] it is displaced by the α olefin and is otherwise inert) and 8.0 mmol of the primary olefin in a small glass pressure vessel joined to a metal pressure head by an O-ring seal. Samples are removed through a small septum. The temperature was controlled to ±0.5 °C with an oil bath. Rates are reproducible usually within the ±10% estimated error range (Table I). We have shown that this reaction is first order in $[Ta]_T$ and, under conditions where K_1 and/or K_2 (eq 1) are large (e.g., for propylene), independent of olefin concentration. The rate of propylene dimerization is also independent of solvent (toluene, decane, ether, chlorobenzene).

(5) The dimerization reactions shown in Table I employed $Ta(\eta^5\text{-}C_5Me_5)$(cyclooctene)$Cl_2$ (0.07 M) as the catalyst; [olefin] = 2.8 M except propylene = 40 psi.

(6) The $k_{obsd} = \{(k_1K_1 + k_2K_2)[ol]\}/\{1 + K_1[ol] + K_2[ol]\}$ assuming that **2** → **4** and **3** → **5** are the slowest steps. By varying the olefin concentration and/or by making several assumptions, we will be able to estimate values for k_1, K_1, k_2, and K_2 in several cases. These data are still being gathered and will be discussed fully later.

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(9) All carbon atoms except those in the two methyl groups furthest from the double bond can be identified (at 67.89 MHz) by peak multiplicity plus empirical chemical shift additivity rules[7] which are known to be (and can be shown to be for several authentic samples here) accurate and reliable for simple hydrocarbons. We estimate that we could see 5–10% of a carbon atom to which no D was attached since it has a significantly different chemical shift at this field strength.

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(11) An alternative explanation which both referees offered is formation of a diene–TaHD complex by a (simultaneous?) double β-hydrogen elimination followed by addition to one double bond to give **12,** all stereospecifically. Phenomenologically the result is the same. We still think our proposed mechanism is more plausible.

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(15) (a) NSF Predoctoral Fellow, 1975–1978. (b) ITP Postdoctoral Fellow (Spain), 1976–. (c) Camille and Henry Dreyfus Teacher–Scholar Grant Recipient, 1978.

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Satellite Structure in the X-ray Photoelectron Spectra of Metal Complexes of Alkyl Isocyanides[1]

Sir:

Shake-up satellite structure[2,3] associated with the X-ray photoelectron spectra (XPES) of transition metal complexes is important because it is frequently related to the energy differences between filled and unfilled molecular orbitals. While such satellites are quite common for salts and complexes of many first-row transition metal ions,[2,3] they have been rarely encountered with the second- and third-row transition metal ions.[2,3] The major exception to this latter experimental observation is the shake-up satellites which are observed in the XPES of certain carbonyls of the second and third transition series.[4-6] For example, satellites seen between 5 and 6 eV on the O 1s, C 1s, and metal (Cr 2p, Mo 3d, or W 4f) levels of $M(CO)_6$, where M = Cr, Mo or W, are believed to be a consequence of a metal(d) → $CO(\pi^*)$ charge-transfer transition.[5] These observations, and their attendant interpretation, naturally lead to the question of whether those molecules which are formally isoelectronic with these carbonyls might exhibit related satellite structure.

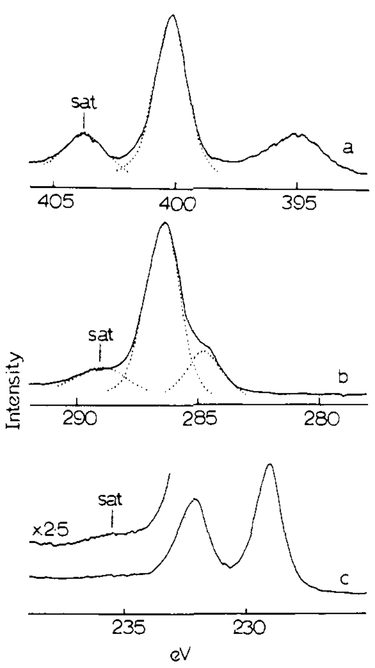

Figure 1. X-ray photoelectron spectra of $[Mo(CNCH_3)_7](PF_6)_2$: (a) N 1s (the Mo $3p_{3/2}$ peak is at 395 eV); (b) C 1s; (c) Mo 3d. Deconvolutions were carried out using the procedure described in ref 11.

In view of the isoelectronic relationship between CO and CNR, the possibility that shake-up satellites might be found in the XPES of transition metal isocyanides makes the latter species of considerable spectroscopic interest. However, while the XPES of certain isocyanide complexes have been reported, for example, $Ni(CNBu^t)_4$, $[M(CNCH_3)_4](PF_6)_2$, and $[M_2(CNCH_3)_6](PF_6)_2$, where M = Pd or Pt,[7-9] such satellites have not previously been detected. We now report the existence of satellites in the XPES of the seven-coordinate molybdenum(II) complexes $[Mo(CNR)_7](PF_6)_2$, where R = CH_3, $C(CH_3)_3$, or C_6H_{11},[10] species which are formally isoelectronic with $Mo(CO)_6$.[13]

The N 1s spectra of all three complexes are virtually identical with the primary photoline at 399.9 ± 0.1 eV (fwhm of 1.5–1.7 eV) and a satellite at 403.6 ± 0.2 eV (Figure 1). The observation of a satellite in the N 1s XPES of all three complexes,[14] the constancy of the intensity ratio I_s/I_p for the satellite and primary photoline (0.18 ± 0.04) and the invariance of the spectra with differences in the X-ray flux and irradiation times makes us confident that we are observing genuine satellite structure rather than the formation of a high oxidation state nitrogen-containing contaminant (such as nitrite).

If the above interpretation is correct, one might expect to find, based on the data for transition metal carbonyls,[5,6] a satellite in the C 1s region of similar magnitude and energy separation from the primary photoline. As shown in Figure 1, this is in fact the case. For $[Mo(CNCH_3)_7](PF_6)_2$, the C 1s

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spectrum exhibits three peaks. That close to 285 eV is due to the usual adventitious carbon "contaminant", while the primary photoline at 286.4 eV can be assigned[8,9,15] to an overlap in the C 1s energies of the cyano and methyl carbons. Since the fwhm value of this peak was not large (1.8 eV), we chose not to deconvolute it. At ~3 eV above the 286.4-eV peak is a satellite whose intensity relative to that of the primary photoline (arising from the two different types of carbon) is ~0.14. Its intensity relative to that of the cyano C 1s peak will be approximately twice this value, thereby making I_s/I_p comparable with the value observed for the N 1s satellite (vide supra). The difference in the positions of the N 1s and C 1s satellites relative to the primary photolines (ΔE ~3.5 eV for N 1s and 3.0 eV for C 1s) may reflect differences in relaxation energy contributions to the chemical shifts.

The C 1s spectra of the *tert*-butyl and cyclohexyl complexes are very similar to that shown in Figure 1 for $[Mo(CNMe)_7](PF_6)_2$, with the exception that there is a marked increase in the intensity of the peak at ~285 eV due to the overlap between the C 1s energies of the aliphatic carbons of the *tert*-butyl and cyclohexyl groups and that due to the adventitious carbon.

The Mo $3d_{3/2,5/2}$ binding energy spectra of the solid complexes ($3d_{3/2}$ at 232.2 ± 0.1 eV and $3d_{5/2}$ at 229.1 ± 0.1 eV) are of a quality comparable with that reported[5] for gas-phase $Mo(CO)_6$, with fwhm values of 1.2–1.4 eV (Figure 1). When the Mo 3d spectrum of $[Mo(CNCH_3)_7](PF_6)_2$ was recorded to high statistics, a very weak feature ($I_s/I_p \approx 0.05$) at ~3.5 eV to the high binding energy side of the primary Mo $3d_{3/2}$ photoline was observed (Figure 1). Three possibilities arise. (1) This is a genuine shake-up satellite associated with the same charge-transfer transition as that giving rise to the N 1s and C 1s satellites. Its position supports this interpretation.[16] (2) It arises from a trace amount of high oxidation state molybdenum oxide contaminant. (3) It is due to a characteristic "plasmon" energy loss. While the two latter possibilities are difficult to eliminate entirely, the dramatic intensity difference between the "satellite" associated with the Mo 3d and N 1s (and C 1s) lines, together with the differences in the satellite position (relative to the primary photoline) in the Mo 3d, N 1s, and C 1s spectra, does not support possibility 3 as the likely explanation.

The similarity of the N 1s and C 1s I_s/I_p ratios for $Mo(CNR)_7^{2+}$ to the O 1s and C 1s I_s/I_p ratios for $Mo(CO)_6$ argues for a similarity in bonding since, as described in detail by Plummer et al.[6] for $M(CO)_6$ species, a decrease in the M–C bond length (i.e., stronger M–CO bonding) will influence both the satellite position relative to the primary peak and the I_s/I_p intensity ratio. The latter becomes smaller the stronger the M–CO (and presumably M–CNR) interaction.

In the case of $Mo(CO)_6$, the lowest energy satellite on the C 1s, O 1s, and metal levels has been assigned[5] to a transition which is predominantly $Mo(d) \rightarrow CO(\pi^*)$. Intense charge-transfer bands in the electronic absorption spectra of $[Mo(CNR)_7]^{2+}$ occur between 4 and 5 eV and may be assignable[17] to the corresponding $Mo(d) \rightarrow RNC(\pi^*)$ transitions. Since the formation of a positive hole upon photoionization lowers the orbital energy of most valence and virtual orbitals, the shake-up energy is usually smaller than that expected on the basis of electronic absorption spectral data. Thus satellites in the 3.0–3.5-eV region for $[Mo(CNR)_7](PF_6)_2$ conform to this expectation. Furthermore, since a $Mo(d) \rightarrow RNC(\pi^*)$ transition involves a virtual orbital which is principally ligand in character, only the C 1s and N 1s satellites should have appreciable intensity since it is the C≡N moiety which is the acceptor species in the shake-up process.[2] The weakness of the Mo 3d satellite supports this assignment, agreeing well with the experimentally observed[5] intensity differences in the XPES of $Mo(CO)_6$. Further analysis must await the results of molecular orbital calculations on such seven-coordinate species. Additional efforts to identify satellite structure in complexes of the heavier transition elements with π-acceptor ligands are currently in progress in our laboratory.

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References and Notes

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Self-Assembly of Molybdenum–Iron–Sulfur Clusters as a Synthetic Approach to the Molybdenum Site in Nitrogenase. Identification of the Major Products Formed by the System $FeCl_3/MS_4^{2-}/C_2H_5SH$ (M = Mo, W)

Sir:

We are currently pursuing a synthetic approach to the Mo site in the FeMo proteins of nitrogenase, more recent preparations of which contain, per 220 000–250 000 daltons, ~2 g-atoms of Mo, 24–33 g-atoms of Fe, and an apparently somewhat smaller quantity of inorganic sulfur than Fe.[1,2] This approach is based on the conclusion from EXAFS analysis that Mo occurs as part of one or two as yet unidentified Mo-Fe-S clusters[3,4] and on the premise that, as with the $[Fe_4S_4(SR)_4]^{2-}$ analogues of ferredoxin sites,[5,6] such clusters, or appropriate precursors thereto, may assemble spontaneously from elementary reagents. We have examined the reaction system $FeCl_3/(R_4N)_2MS_4/EtSH$ (M = Mo, W) in alcohol solvents in some detail. Here we document that the principal Mo-containing products formed by this system are the "double-cubane" complexes I ($[Mo_2Fe_6S_9(SEt)_8]^{3-}$), II ($[Mo_2Fe_6S_8$-

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