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Contribution from the Department of Chemistry,
University of California, Los Angeles, California 90024

Photochemistry of Azidopentacarbonyltungstate(0)[1]

R. MARC DAHLGREN[2] and JEFFREY I. ZINK*[3]

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Three photoreactions are observed when the lowest energy excited state (436 nm) of the $W(CO)_5N_3^-$ anion is irradiated. For the PPN salt, coordinated nitrene formation leads to the production of $W(CO)_5NCO^-$ in the presence of added CO ($\Phi = 0.06$). For the $AsPh_4$ salt, a complex series of secondary thermal reactions leads to a noncarbonyl product ($\Phi = 0.07$). The stereochemistry of the CO substitution is investigated with labeling experiments. The photoactive excited state is assigned to an admixture of both azide to metal charge transfer and ligand field character on the basis of electronic, magnetic circular dichroism, vibrational, and emission spectra. The photochemistry is interpreted in terms of the charge transfer and ligand field character of this state, and a model of the excited-state potential surface is proposed.

The coordinated azide ligand has been the subject of many photochemical investigations.[4-10] Three modes of photodecomposition of the N_3 moiety have been observed. Azide complexes of Pt(II),[4] Au(III),[5] and $Co^{III}(NH_3)_5N_3^{2+}$ [6] exhibited photoredox chemistry resulting in the production of azide radicals. For the series of azidopentaammines of Co(III),[6] Rh(III),[7] and Ir(III),[7] photoredox in Co(III) was replaced by coordinated nitrene formation as the dominant mode of azide photodecomposition in Rh(III) and Ir(III). Although $Cr^{III}(NH_3)_5N_3^{2+}$ was initially believed to demonstrate predominantly photoredox chemistry,[8] recent work indicated that nitrene formation is dominant.[9] In contrast to the ammine complexes, the azidopentacyanides of Rh(III) and Ir(III)[10] photoaquated, eliminating azide as the anion, N_3^-.

We have introduced a model based on relative bonding changes in the coordinated azide ligand in the excited state as assessed by EHMO–SCC calculations which accounts for the observed trend from photoredox to nitrene formation in the Co, Rh, Ir triad.[11] For charge-transfer and ligand-localized excited states, these calculations predicted large changes in the internal azide nitrogen–nitrogen bond orders. These changes were a function of the overlap between the metal and the azide nitrogen atom. Ligand to metal charge transfer (LTMCT) and ligand localized (LL) states produced destabilization of the bond between the metal-bound nitrogen and the terminal N_2 which maximized for large metal–azide overlap. It is in these cases, such as third-row transition-metal–azide complexes, where coordinated nitrene photointermediates are anticipated.

The objectives of this investigation are to determine the modes and efficiency of the photochemical reactions of $W(CO)_5N_3^-$ from its lowest energy excited state and to describe the nature of this state through spectroscopic analysis. This is the first quantitative study of the photochemistry of a zerovalent, third-row azidometal carbonyl, a type of complex from which metal–nitrene intermediates are expected to result from a LTMCT state.[11] From the photochemical results, a model of the excited state is developed which is compared with other metal azides and the well-developed photochemistry of $W(CO)_5L$ complexes.[12-14]

Results

Spectroscopy. 1. UV–Visible and Magnetic Circular Dichroism Spectra. Both the electronic absorption and magnetic circular dichroism (MCD) spectra of $[AsPh_4][W(CO)_5N_3]$ are shown in Figure 1. The low-energy region of the absorption spectrum is dominated by an intense peak at 2.45 μm^{-1} (408.5 nm, ϵ 2900 $M^{-1}\ cm^{-1}$) with a red shoulder at approximately 2.19 μm^{-1} (457.3 nm) and is remarkably similar to the previously reported spectrum of $[NEt_4][W(CO)_5Br]$[14] where the major band is at 2.44 μm^{-1} (ϵ 2500 $M^{-1}\ cm^{-1}$) with a shoulder at 2.21 μm^{-1}. These absorption features in both complexes are red shifted relative to similar bands in $W(CO)_5$(ammine) compounds where the peaks occur at 2.53 and 2.31 μm^{-1}.[14] For $[AsPh_4][W(CO)_5N_3]$ there is no hypsochromic shift of the major band at 2.45 μm^{-1} upon changing the solvent from $CHCl_3$ to either MeOH, EPA, or propylene carbonate, nor is this band very cation dependent: Li salt, $E_{max} = 2.45\ \mu m^{-1}$; Na salt, $E_{max} = 2.43\ \mu m^{-1}$; $AsPh_4$ salt, $E_{max} = 2.45\ \mu m^{-1}$; PPN (=$\mu$-nitrido-bis(triphenylphosphorus) cation) salt, $E_{max} = 2.45\ \mu m^{-1}$. In the 77 K absorption spectrum, a new feature is resolved at approximately 2.33 μm^{-1} (430 nm) which also appears in the low-temperature spectrum of $W(CO)_5I^-$ and $W(CO)_5Br^-$ but is not evident for any $W(CO)_5$(ammine) complexes.

The MCD spectrum of $W(CO)_5N_3^-$ (Figure 1) has a well-resolved s-shaped feature associated with the 2.45 μm^{-1} band of the electronic spectrum. As the energy of the null of the MCD corresponds to the maximum of the electronic feature, this MCD band is assigned as an *A* term of positive sign. Again there is a striking similarity between this MCD spectrum and preliminary MCD results for $W(CO)_5X$ (X = halides and ammines).[15]

2. Emission Spectra. Low-temperature (77 K) emission spectra were obtained for the $AsPh_4$ and PPN salts of $W(CO)_5N_3^-$ in the solid state, in suspensions in 2-MeTHF glasses, and in 4/1 v/v EtOH/MeOH glasses. Identical spectra were obtained under all conditions with the emission maximum at 1.945 μm^{-1} (514 nm) when excited at 2.50 μm^{-1} (400 nm). The maxima are slightly blue-shifted from those previously reported for $W(CO)_5L$ (L = ammines and phosphines) which all emit at 1.88 μm^{-1} (530 nm).[13,14,16] The observed lifetime of $[PPN][W(CO)_5N_3]$ is 10.6 ± 1 μs in a 4/1 EtOH/MeOH glass at 77 K, intermediate between the lifetimes of substituted pyridine derivatives of $W(CO)_6$ ($\tau \simeq 30\ \mu s$)[13] and ammine and phosphine derivatives ($\tau \simeq 1\text{–}5\ \mu s$).[16]

3. Vibrational Spectra. The proposed assignments of the carbonyl region infrared absorption bands of $W(CO)_5N_3^-$ in

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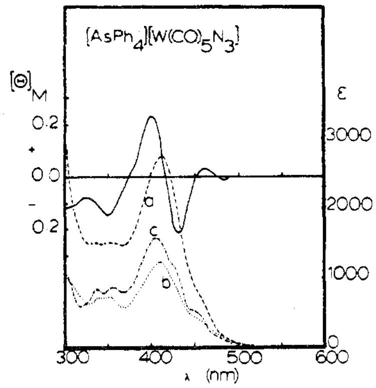


Figure 1. Optical and magnetic circular dichroism spectra of $[AsPh_4][W(CO)_5N_3]$: (a) MCD and optical spectra in CH_3Cl at 300 K; (b) EPA at 300 K; (c) EPA at 77 K (uncorrected for volume contractions).

Table I. Disappearance Quantum Yields of $W(CO)_5N_3^-$ under Various Conditions of Temperature, Solvent, and Cation[a]

reaction	cation	solvent	temp, °C	Φ_{DIS}[b]
A	PPN	$CHCl_3$[c]	−6	0.027
B	PPN	$CHCl_3$[c]	−6	0.06[d]
C	PPN	$CHCl_3$[c]	28	0.062
D	PPN	MeOH[c]	7	0.016
E	$AsPh_4$	$CHCl_3$[c]	7	0.071
F	$AsPh_4$	$CHCl_3$[e]	7	0.085
G	$AsPh_4$	MeOH[c]	7	0.037
H	$AsPh_4$	MeOH[e]	7	0.050
I	$AsPh_4$	Me_2SO[c]	10	0.018

[a] Photolysis at 436 nm. [b] The quantum yield is based on the disappearance of the 408-nm band in the UV-visible spectrum. The experimental uncertainty is ±10%. [c] Solvent saturated with CO gas. [d] Initial formation Φ of $W(CO)_5NCO^-$ after correcting for secondary photolysis and inner filtering. [e] N_2-saturated solvent.

$CHCl_3$ are as follows: 2084 cm^{-1}, $\nu(CO)$ $A_1^{(1)}$; 1922 cm^{-1}, $\nu(CO)$ E; 1849, $\nu(CO)$ $A_1^{(2)}$; 2048 cm^{-1} $\nu(\text{sym } N_3)$. Carbon–oxygen force constants (k_1 (trans CO), 13.95 mdyn/Å; k_2 (cis CO), 15.74 mdyn/Å; k_i, 0.41 mdyn/Å) were calculated using the Cotton–Kraihanzel approximation.[17] Both cis and trans carbonyl ligands have much lower bond orders than those of corresponding ammine and phosphine derivatives.[14] The Graham $\Delta\sigma$ and $\Delta\pi$ parameters[18] ($W(CO)_5N_3^-$: $\Delta\sigma = 1.03$ mdyn/Å, $\Delta\pi = -1.04$ mdyn/Å, relative to L = cyclohexylammine: $\Delta\sigma = \Delta\pi = 0$) imply, as expected, that the N_3^- ligand is a better π donor and poorer σ donor toward $W(CO)_5$ than is cyclohexylammine.

Photochemistry. The quantum efficiencies and photoproduct distributions for 436-nm photolysis of [cation][$W(CO)_5N_3$] is a strong function of the cation,[19] the solvent, and the temperature. Table I sets out the quantum yields for the disappearance of the 408-nm absorption, characteristic of $W(CO)_5N_3^-$, under these various conditions. When the lithium, sodium, and PPN salts are photolyzed in CO-saturated solvent, quantitative conversion to a mixture of $W(CO)_5NCO^-$ and $W(CO)_6$ results. However, photolysis of the $AsPh_4$ salt, under similar conditions, leads to neither of these products (vide infra). Raising the temperature from −6 to +34 °C approximately doubles the quantum yield (reactions A and C of the table) which is similar to the temperature effect observed in other systems.[20] In a given solvent, the quantum efficiency of the $AsPh_4$ salt always exceeds that of the PPN salt (reactions C and E and reactions D and G). For both salts, the solvent dependence of the quantum yields follows the order $CHCl_3 > MeOH > Me_2SO$ (for $AsPh_4$).

1. [PPN][$W(CO)_5N_3$]. During photolysis in CO-saturated $CHCl_3$ at −6 °C, bands at 2236 cm^{-1}, corresponding to the NCO vibration in $W(CO)_5NCO$, and at 1985 cm^{-1}, corresponding to the $W(CO)_6$ T_{1u} vibration, grow in. The 2084-cm^{-1} $\nu(CO)$ $A_1^{(1)}$ $W(CO)_5N_3^-$ and the 2049-cm^{-1} coordinated N_3 bands disappear while new absorptions are observed at 2069 cm^{-1} ($W(CO)_5NCO^-$ $\nu(CO)$ $A_1^{(1)}$) and 1843 cm^{-1} ($W(CO)_5NCO^-$ $\nu(CO)$ $A_1^{(2)}$) in the 21 h spectrum. No feature indicative of free N_3^- is present at 2026 cm^{-1} at any time during the photolysis.

By utilization of the molar absorptivities of the $W(CO)_5NCO^-$ 2236-cm^{-1} band and the 2049-cm^{-1} coordinated azide feature, the percent of conversion of $W(CO)_5N_3^-$ to $W(CO)_5NCO^-$ can be calculated as a function of irradiation time. For 436-nm photolyses of less than 5-min duration, corresponding to about 1% disappearances of $W(CO)_5N_3^-$, greater than 90% of the photoproduct is the isocyanate. After 4 h, NCO formation decreases to 22% and then to 17 and 10% of the product for 7 and 21 h of photolysis, respectively. Because the electronic spectra of $W(CO)_5N_3^-$ and $W(CO)_5NCO^-$ are extremely similar with identical molar absorptivities at 436 nm, these data strongly suggest that secondary photolysis of $W(CO)_5NCO^-$, the primary photoproduct, is occurring.

[PPN][$W(CO)_5NCO^-$] is cleanly converted to $W(CO)_6$ + NCO^- when irradiated at 436 nm in CO-saturated $CHCl_3$ at −6 °C as evidenced by the appearance of the $W(CO)_6$ T_{1u} IR feature and an isosbestic point at 375 nm in the electronic spectrum. The quantum yield of this reaction is 0.009. Hence, [PPN][$W(CO)_5N_3$] is first photochemically converted to [PPN][$W(CO)_5NCO^-$] which then produces $W(CO)_6$ as the secondary photolysis product.

The quantum yields for reactions A, C, and D in the table are calculated for the total disappearance of the 408-nm band. They represent the lower limit for the $W(CO)_5NCO^-$ product yield. An upper limit of this yield was calculated by weighting the fractional disappearance of the 408-nm band by the percent of conversion of azide to isocyanate during a given period of photolysis as determined from the infrared analysis. This procedure results in a quantum yield of 0.06 for the primary production of $W(CO)_5NCO^-$ (Table I, reaction B). Hence, the observed increase in the quantum yields of the $AsPh_4$ system relative to the PPN salts (table) is an artifact of the secondary photolysis of the $W(CO)_5NCO^-$ photoproduct which is not formed in the $AsPh_4$ system (vide infra).

When [PPN][$W(CO)_5N_3$] is photolyzed at 436 nm in a 10^{-2} M PPh_3 solution in $CHCl_3$ at −6 °C with no added CO, the coordinated azide as well as the $W(CO)_5N_3^-$ CO vibrations disappear, and no NCO nor free N_3^- bands appear. New carbonyl bands are observed at 2075 (w), 2021 (m), 1902 (s), and 1821 (m) cm^{-1} suggesting a cis disubstituted product (not *cis*-$W(CO)_4(PPh_3)_2$). The photoproduct is tentatively suggested to be *cis*-$W(CO)_4(PPh_3)(N{=}PPh_3)^-$[21] based on the four-band carbonyl pattern and the disappearance of N_3 vibrations. The PPN cation obscures the PN vibrational region of the infrared which would contain the triphenylphosphinimide ligand bands. The absence of an isocyanate product clearly indicates that the mechanism for formation of $W(CO)_5NCO^-$ is intermolecular and therefore supports a coordinated nitrene photointermediate.

2. [$AsPh_4$][$W(CO)_5N_3$]. A 436-nm photolysis of [$AsPh_4$][$W(CO)_5N_3$] results in a new mode of photoreactivity. During irradiation, all bands in the carbonyl region of the infrared disappear at the same rate as the 408-nm electronic absorption. Upon prolonged photolysis, all infrared and the electronic absorptions at λ > 250 nm cease, and a white precipitate is observed. The rate of disappearance of the coordinated-N_3 IR stretch is the same as that of the $AsPh_4$ cation vibration at 1187 cm^{-1}. Qualitative analysis of the white precipitate shows that it contains As and W. This substance has no infrared absorption in the carbonyl region indicating that it is the end product of a complex chain of secondary reactions leading from an unstable photointermediate. It was not further characterized.

The white precipitate may be produced in the absence of irradiation by the reaction of $[AsPh_4][W(CO)_5N_3]$ with benzoyl peroxide, a radical initiator and strong oxidant. Changes in the UV–visible and infrared spectra qualitatively similar to those observed during photolysis were observed when benzoyl peroxide, Cl_2 gas, or phosgene was added to MeOH or $CHCl_3$ solutions of $[AsPh_4][W(CO)_5X]$ (X = N_3, Br, I, or NCO) but were not observed when the reaction was tried with the PPN salt. A similar degradation occurred thermally, without addition of these reagents after several hours. A recent investigation of the photochemistry of $[AsPh_4][Mn(CO)_5]$ demonstrated that ligand photodissociation led to oxidative addition of $AsPh_4^+$ to the coordinatively unsaturated Mn intermediate forming *cis*-$Mn(Ph)(AsPh_3)(CO)_4$,[22] which may implicate this reaction in the tungsten system.

To test if carbon monoxide photosubstitution occurs in $W(CO)_5N_3^-$, $[AsPh_4][W(CO)_5N_3]$ was photolyzed at 436 nm in a sealed tube pressurized with ^{13}CO and analyzed by ^{13}C FTNMR. Because the coordinated azide reaction stoichiometrically eliminates the $AsPh_4$ cation from solution as the white precipitate, the relative amount of enrichment in the cis and trans positions of the remaining $W(CO)_5N_3^-$ may be calculated as a ratio of the intensity of the ^{13}CO resonance to that of the $AsPh_4^+$ resonances. Before photolysis, only the cis CO signal is detectable above the baseline with intensity 0.09 (intensity of the cis CO resonance/intensity of the 132.68-ppm $AsPh_4$ resonance). After photolysis, both the cis (intensity 3.00) and trans (intensity 0.15) carbonyls are detected in a ratio of 19.5:1 (cis:trans). This sample was freeze–pump–thawed to remove all excess ^{13}CO, natural-abundance CO was introduced, and photolysis was continued. The intensity of the cis CO resonance is reduced to 2.65 while the trans CO intensity rises to 0.28. The ratio (cis:trans) is reduced to 9.56:1. Barring the unlikely possibility that cis-labeled $W(CO)_5N_3^-$ is selectively photodecomposed to the white precipitate, these data necessitate a mechanism allowing for the net transport of a cis label to a trans position.

To obtain a quantum yield for the ligand photosubstitution reaction, $[AsPh_4][W(CO)_5N_3]$ was photolyzed in N_2- and CO-saturated $CHCl_3$ and MeOH (reactions E and F and G and H of the table). In both the N_2- and CO-saturated solvents, an isosbestic point is observed at 475 nm.[23] The quantum yield difference between the N_2- and CO-saturated solvent is the same (0.013) in both $CHCl_3$ and MeOH and thus represents an upper limit to the CO substitution quantum yield.

Discussion

Lowest Energy Excited State. The low-energy absorption feature of $W(CO)_5N_3^-$ at 2.45 μm^{-1} is assigned to the degenerate $^1A_1 \rightarrow {}^1E$ transition on the basis of the *A* term in the MCD spectrum. The small red shoulder which disappears in the analogous chromium bromide complex is assigned to the spin–orbit manifold arising from the ^3E state. In accord with previous MCD work on $Mn(CO)_5Br$,[24] isoelectronic with $W(CO)_5N_3^-$, the positively signed *A* term is consistent with population of a d_{z^2} metal orbital which is thus the lowest unoccupied molecular orbital in this complex. The MCD spectrum supports an ^1E state arising from either a LTMCT state (N_3, $\pi_{nb} \rightarrow d_{z^2}$) or a LF state ($d_{xz}$, $d_{yz} \rightarrow d_{z^2}$) as the lowest energy spin allowed transition.

A low-energy LTMCT state is consistent with the azide ion's low optical electronegativity of 2.8 (equal to that of Br^-).[25] The photoelectron spectrum (PES) of $Mn(CO)_5Br$ indicates that the highest occupied molecular orbital (HOMO) is primarily Br p_π in character with an ionization energy of 8.86 eV.[26] The PES of $W(CO)_6$ shows that the HOMO is the metal 5d orbital at 8.56 eV.[27] If the energies of the Br^- p_π and N_3^- π_{nb} levels are taken as approximately equal on the basis of their optical electronegativities, the HOMO of $W(CO)_5N_3^-$ is almost certainly not primarily N_3^- π_{nb}, because the increased charge on the tungsten center should raise its d-orbital energies relative to manganese. The azide orbital of e symmetry must be energetically close to the HOMO. These conclusions are consistent with those of McLean for the anionic tungsten pentacarbonyl halides.[28]

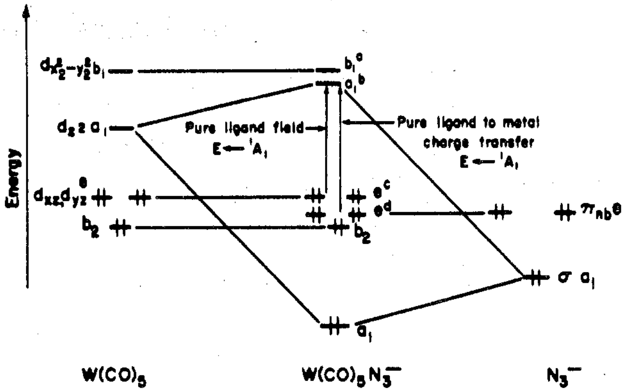


Figure 2. One-electron molecular orbital diagram for the $W(CO)_5N_3^-$ ion. The metal–ligand bonding character of the orbitals is as follows: (a) metal–CO σ antibonding in the *xy* plane; (b) metal–N_3 and metal–CO σ antibonding along the unique axis; (c) metal–N_3 π antibonding; (d) metal–CO π bonding principally along the unique axis.

The additional electronic absorption feature resolved at low temperature for $W(CO)_5X^-$ (X = I^-, Br^-, and N_3^-) but not for complexes with lowest energy LF states may be direct evidence for the azide to tungsten state. An azide to metal LTMCT band should be of very low intensity.[29] However, the new 2.33-μm^{-1} band cannot be definitively assigned to the LTMCT state because of the possibility that it is a vibrational component of the LF transition.

A one-electron molecular orbital scheme consistent with these data is shown in Figure 2. The repulsion of the (d_{xz}, d_{yz}) orbitals of e symmetry by the N_3 π_{nb} orbitals of e symmetry and the π-donor ability of N_3^- account for the observed red shift of the $^1A_1 \rightarrow {}^1E$ transition relative to $W(CO)_5$(ammine) complexes. The close proximity of the filled azide π orbitals to the low-lying metal d orbitals suggests that the lowest energy excited state of this complex is primarily LF in character but contains a large component of LTMCT.

Photochemistry of $W(CO)_5N_3^-$. $W(CO)_5N_3^-$ undergoes three reactions when irradiated in its lowest energy absorption band in solution: reaction of the coordinated azide (eq 2),

$$W(CO)_5N_3^- \xrightarrow{h\nu} [W(CO)_5N_3^-]^* \qquad (1)$$

$$[W(CO)_5N_3^-]^* \xrightarrow{-N_2} [W(CO)_5N^-] \xrightarrow{CO} W(CO)_5NCO^- \qquad (2)$$

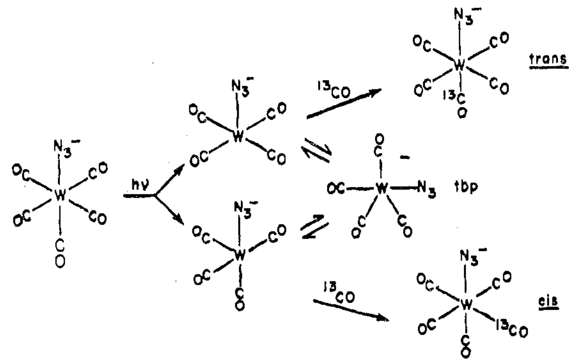
$$[W(CO)_5N_3^-]^* \xrightarrow{AsPh_4^+} \rightarrow \text{rapid thermal loss of CO's} \qquad (3)$$

$$[W(CO)_5N_3^-]^* \xrightarrow{-CO} W(CO)_4N_3^- \xrightarrow{L} W(CO)_4(L)(N_3)^- \qquad (4)$$

reaction with $AsPh_4^+$ (eq 3), and carbonyl labilization (eq 4). Photolabilization of the azide ion or the azide radical is not observed.

The photoproduction of coordinated isocyanate results from the intermolecular reaction of CO with a coordinated nitrene

Scheme I



which forms from a state with significant LTMCT character. Loss of terminal N_2 leads to a nitrene stabilized by back-bonding to the electron rich metal, which scavenges CO to form isocyanates[30] and takes up PPh_3 to form coordinated triphenylphosphinimido complexes.[21] A similar mechanism was suggested for the photochemistry of $Mo^{II}Cp(CO)_2(PPh_3)(N_3)$.[31] The wavelength dependence of nitrene photoproduction from other metal azides[8b] indicated a threshold energy for nitrene production precluding its formation from LF states. These observations are in accord with the predictions of our MO model.[11]

The reaction with $AsPh_4^+$ (eq 3) produces an insoluble product which does not contain carbon monoxide, azide, or isocyanate. The product is many steps removed from the primary photochemical step. Thus, this product cannot be used to infer the excited-state origins of this reaction.

The ligand exchange path, eq 4, results from the increased σ antibonding in the excited state. Dissociative loss of CO, as in the LF photochemistry of other $W(CO)_5L$ complexes,[12,14] produces a 16-electron coordinatively unsaturated intermediate which scavenges a free ligand to form the observed 18-electron products.

The ^{13}CO labeling experiments provide the opportunity to study the LF photochemistry of $W(CO)_5N_3^-$ independent of the azide photodecomposition. The cis ^{13}CO labeling of the azide complex exceeds the 4:1 statistical ratio. These results are similar to those observed for the thermal[32] and photochemical[14,33] labeling of $W(CO)_5$(phosphine) complexes, although the efficiency ($\Phi = 0.013$) is much lower. These results are in contrast to the stereospecific cis enrichment observed for $M(CO)_5$(ammine) (M = Cr, Mo, W).[34]

The absence of stereospecificity in the azide material means that rearrangement must be considered. When the enriched $W(CO)_5N_3^-$ is photolyzed with ^{12}CO, the transport of a cis label to a trans position is observed. A mechanism for this observed transport is suggested in reaction Scheme I. CO photosubstitution in similar systems has been shown experimentally[35] and theoretically[36] to occur through a square-pyramidal (SP) intermediate. Rearrangement of the azide ligand from an apical to a basal position on this SP, through a trigonal-bipyramidal intermediate, would scramble any labels between the cis and trans positions. The NMR results require that this rearrangement process be faster than the rate of recombination of the SP intermediate with CO. Therefore, the relative rates of cis and trans CO photodissociation cannot be determined.

A Model of the $W(CO)_5N_3^-$ Excited-State Potential Surface. The high degree of configuration interaction between the LF and LTMCT excited states and the different modes of LF and LTMCT photochemistry of $W(CO)_5N_3^-$ provide the basis for a model of the potential surface of the lowest energy excited state as shown in Figure 3. This potential surface has two reaction channels, one along a mode which separates terminal N_2 from the coordinated nitrene and another which separates carbon monoxide from $W(CO)_4N_3^-$. Progress along the former mode (CT vector) leads to a state with increasing LTMCT character while along the latter route (LF vector) a pure LF state is reached. As both the pure LF and LTMCT electronic states are of E symmetry, the surfaces associated with wells A and B may not cross, and hence there is a low-energy saddle point, C, linking the two wells.

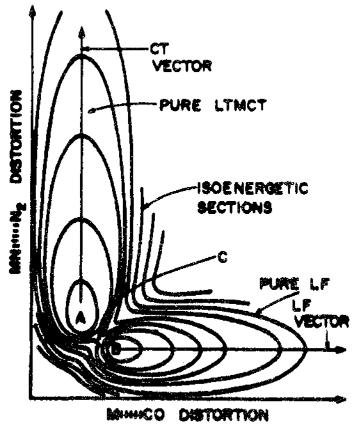


Figure 3. An empirical model of the excited-state potential energy surface of the $W(CO)_5N_3^-$ ion.

Experimentally, the lowest energy reaction channel is along the CT vector ($\Phi = 0.07$ for azide photodecomposition compared to $\Phi = 0.01$ for CO substitution). The low barrier along the CT vector is also in accord with both the EHMO–SCC calculations,[11] which predict considerable internal azide bond weakening in the pure LTMCT state, and with the concept of stability associated with a nitrene bound to an electron rich metal center such as $W(CO)_5$. The latter point may be of central importance for $M(CN)_5N_3^{3-}$ (M = Rh(III), Ir(III)) where there is less available metal π-electron density, and the radial extent of the π orbitals on the metal is reduced relative to these tungsten materials. Nitrene intermediates are not generated photochemically in these cyanide derivatives.[10]

Of the two local minima in this surface, point B must be lower in energy than point A. The luminescence, which originates from the lowest point on this surface, is qualitatively similar to that observed from other $W(CO)_5L$ complexes where there is only an LF well in the lowest energy potential surface. Thus, the emission is more LF than LTMCT in nature and originates from well B rather than well A. The longer luminescence lifetime (compared to $W(CO)_5$(ammine)) may result either from the absence of higher energy vibrations in the molecule contributing to nonradiative processes[37] or from partitioning of energy between wells A and B.[38]

Motion along the LF vector leads to CO substitution but not N_3^- loss. As noted in Figure 2, the axially metal–azide π antibonding and metal–CO π bonding d_{xz} and d_{yz} orbitals are depopulated in the LF state. The net metal–N_3^- bond weakening is less than that experienced by non-π-interacting ammine ligands while metal–CO bond weakening remains about the same. The CO photosubstitution reaction occurs along the LF vector with about the same quantum yield as in tungsten carbonyl ammines.[14] Azide photolabilization does not occur because of the increased π bonding. All azide reactivity occurs along the lower energy CT escape route (CT vector) in Figure 3.

Experimental Section

1. Preparation and Characterization of Compounds. These tungsten carbonyl derivatives were prepared in Schlenk apparatus under prepurified N_2 until after the addition of either the PPN or $AsPh_4$ cations.

[AsPh$_4$][W(CO)$_5$W$_3$].[39] Anal. Calcd for $WC_{29}H_{20}O_5N_3As$: C, 46.48; H, 2.70; W, 24.54; N, 5.61. Found: C, 46.22; H, 2.57; W, 24.80; N, 4.89. Reported carbonyl IR[39] (cm^{-1}): 2076, 2040 (N$_3$), 1914, 1853. Found (cm^{-1}, CHCl$_3$ solution): 2084, 2048 (N$_3$), 1922, 1849.

[AsPh$_3$][W(CO)$_5$NCO].[40] Anal. Calcd for $WC_{30}H_{20}O_6NAs$: C, 48.09; H, 2.70; N, 1.87. Found: C, 47.73; H, 2.48; N, 1.58. Reported carbonyl IR[40] (cm^{-1}, acetone): 2230 (NCO), 2062, 1915, 1854. Found (cm^{-1}, CHCl$_3$): 2236 (NCO), 2069, 1921, 1843.

[PPN][Cl][41] was used to prepare [PPN][N$_3$] by metathesis.

[PPN][W(CO)$_5$N$_3$]. W(CO)$_6$ (1.00 g) was irradiated for 1.5 h with a PEK-110 Hg source in 100 mL of purified THF under constant N$_2$ purge. [PPN][N$_3$] (0.45 g) in 50 mL of acetone was added to this yellow solution at room temperature, and it was immediately rotary evaporated to a yellow oil at 35 °C. The oil was suspended in 20 mL of EtOH, filtered, and evaporated. The residue was dissolved in 25 mL of boiling EtOAc which was slowly cooled to 0 °C producing a light yellow precipitate. The yellow solution was decanted into 150 mL of pentane which formed an oil on the bottom of the vessel. The oil, [PPN][W(CO)$_5$N$_3$], was washed with additional pentane and vacuum-dried for 2 days resulting in a solid containing 5% W(CO)$_6$ as an impurity. Carbonyl IR (cm^{-1}, CHCl$_3$): 2084, 2049 (N$_3$), 1985 (W(CO)$_6$), 1922, 1849.

[PPN][W(CO)$_5$NCO]. [PPN][W(CO)$_5$N$_3$]) (0.5 g) was refluxed in 100 mL of CO-saturated EtOH for 1 h after which the solution was reduced to 10 mL and was cooled to room temperature. The product was precipitated by the slow addition of H$_2$O and collected by filtration followed by several water washes. Anal. Calcd for $WC_{24}H_{30}N_2P_2O_6$: C, 55.77; H, 3.35; N, 3.10; W, 20.33. Found: C, 54.60; H, 3.36; N, 3.27; W, 20.06. Carbonyl IR (cm^{-1}, CHCl$_3$): 2236 (NCO), 2069, 1921, 1843.

[Li]- and [Na][W(CO)$_5$N$_3$] were prepared by addition of a stoichiometric amount of the azide salt in 25 mL of MeOH to a solution of 0.25 g of W(CO)$_6$ in 25 mL of THF irradiated as described above. The solution was evaporated to 5 mL, filtered, and eluted down a 1-ft silica gel column with CHCl$_3$. The first yellow band was collected. IR bands at 2084, 2049 (N$_3$), 1922, and 1855 cm^{-1} confirmed the presence of W(CO)$_5$N$_3^-$.

2. Photochemistry. All solvents were distilled under N$_2$ before use, and the 1-cm cells used for photolysis were sealed with septum caps. CO gas was purified by successively passing it through 5 M H$_2$SO$_4$, KOH pellets, and Celite cooled to −80 °C. Actinometry was accomplished with K$_3$Fe(C$_2$O$_4$)$_3$[42] on the 436-nm Hg line of a 1000-W high-pressure Hg source as described previously,[14] resulting in average intensities over the cell surface of 1.8×10^{15} photons/s. The temperature was maintained at ±1 °C by circulating EtOH from an Aminco 4-8600 constant-temperature bath through a brass cell holder. The initial absorption of the 436-nm band by the samples was determined by passing the light through the sample and into a 0.25-m Jarrell-Ash monochromator equipped with a photomultiplier tube and recording the light intensity as a function of wavelength. A Beer's law plot was constructed to arrive at the molar absorptivity of the starting materials at 436 nm using the fractional transmittance of the samples compared to pure solvent.

The following relationship was used to calculate the quantum yield,

$$A_t + \frac{1}{2.303\epsilon}[\ln(1 - e^{-2.303\epsilon A_t})] = -\frac{\Phi I_0}{NV}t + \left[A_0 + \frac{1}{2.303\epsilon}\ln(1 - e^{-2.303\epsilon A_0})\right]$$

Φ, where I_0 is the light intensity (photons/s), t is the irradiation time (s), N is Avogadro's number, V is the cell volume (L), ϵ is the molar absorptivity of the reactant at 436 nm [L/((mol)(cell path length))], and A_t and A_0 are the concentrations of the reactant at times t and zero (M). A_t was determined from the intensity diminution of the 408-nm absorption. The left side of this relationship was plotted as a function of time, and Φ was derived from the slope. Identical Φ values were obtained when the data were analyzed in our iterative least-squares fitting program described previously.[14]

3. ^{13}CO Labeling Experiments. A 90.5 atom % ^{13}CO sample (Merck Lot F128) was transferred to a Pyrex tube containing 10 mL of a saturated CDCl$_3$ solution of [AsPh$_4$][W(CO)$_5$N$_3$] with a Toepler pump. The tube was sealed and irradiated at 436 nm through the Pyrex walls with constant magnetic stirring.

4. MCD Spectroscopy. The MCD spectrum was obtained by Professor A. F. Schreiner[15] using a spectrometer described previously.[43]

5. Vibrational, Electronic, and Emission Spectroscopy. Infrared spectra in 4.5–5.65-μm region were obtained with a Beckman IR-4. A Perkin-Elmer Model 521 was used for other IR ranges. UV–visible spectra were recorded on Cary-11 and Cary-14 instruments. Low-temperature luminescence measurements were obtained with a Spex Fluorolog modified for low-temperature work.[14] 2-MeTHF was triply distilled under N$_2$ while the alcohol mixture was used directly after N$_2$ purging. The lifetimes were determined using the low-temperature sample holder.[14] 400-nm pulses of less than 2 ns from a Molectron N$_2$ dye laser were used for excitation. The emission was passed through a Jarrell-Ash 0.5 m monochromator tuned to 533 nm and detected with a 9502 (S response) photomultiplier tube. The signal was digitized and accumulated with a DEC PDP 11/45 computer system at 0.2 μs intervals. Log (intensity) plots yielded the lifetime.

6. ^{13}C FTNMR Spectra. ^{13}C NMR spectra were obtained with a Varian CFT-20 instrument. CDCl$_3$ solvent was used to provide a ^{2}H lock signal, and 0.1% w/v Cr(acac)$_3$ was added to the samples as a relaxation agent. For these saturated solutions of [AsPh$_4$]-[W(CO)$_5$N$_3$], accumulation times of 1.023 s with a pulse delay of 1.977 s and a pulse width of 10 μs (pulse angle ~45°) resulted in high signal to noise ratios for the carbonyl resonances after the collection of ~10 000 transients.

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Registry No. [AsPh$_4$][W(CO)$_5$N$_3$], 26606-46-2; [PPN][W(CO)$_5$N$_3$], 63363-64-4; [AsPh$_4$][W(CO)$_5$NCO], 15407-42-8; [PPN][W(CO)$_5$NCO], 57196-22-2; [Li][W(CO)$_5$N$_3$], 68645-85-2; [Na][W(CO)$_5$N$_3$], 68645-84-1; W(CO)$_6$, 14040-11-0.

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Contribution from the Department of Chemistry,
University of Texas, Austin, Texas 78712

Ground States of Molecules. 52.[1] A MNDO SCF–MO Study of the Coordination of Beryllium–Indenyl and –Fluorenyl Complexes

MICHAEL J. S. DEWAR* and HENRY S. RZEPA

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MNDO SCF–MO calculations have been carried out for the "half-sandwich" complexes formed between mono- and dibenzocyclopentadienyl anions (indenyl and fluorenyl, respectively) and BeH^+ or $BeCl^+$. Three stable isomers were located for the indenyl complexes, the calculated energies increasing with the coordination $\eta^1 > \eta^5 > \eta^6$. For the fluorenyl/BeH system, no minimum corresponding to an η^5 isomer could be located, and the 9-η^1 species was again lower in energy than the η^6 isomer. The calculated structure of the latter compound showed interesting similarities with the observed crystal structure of (η^5-cyclopentadienyl)(η^6-fluorenyl)iron.

Introduction

While an immense amount of work has been carried out on "sandwich" and "half-sandwich" complexes of transition metals, and while many of these compounds are of major technological interest and importance, few quantitative theoretical treatments of them are yet available.[2] Even the simplest compounds of this class contain too many electrons to be treated adequately by current ab initio procedures, particularly since the R–H (Roothaan–Hall[3]) method is known to be unsatisfactory for nonclassical species of this type if a minimum orbital basis set is used. Conventional semiempirical methods (EH, CNDO, INDO) are quite unsuitable for quantitative studies, while MINDO/3[4] or the more recently developed MNDO[5] have not yet been parametrized for transition metals, or indeed for compounds where d AO's are involved in bonding. There is, however, one metal which can form π complexes which contain only a few electrons and which has no d AO's in its valence shell, i.e., beryllium. Here ab initio calculations of fairly high quality are possible, although they are limited as yet to simple systems and are very rarely carried out with any geometry optimization because of the prohibitive cost it would entail. Now the group RBe, where R is a monofunctional ligand, resembles groups such as $Cr(CO)_3^-$ or $Mn(CO)_3$ (with vicinal carbonyls) in being a triple acceptor and in forming complexes of the type AX_3 with analogous geometries, the ligands X being equivalent and lying at the corners of an equilateral triangle. It therefore seems likely that half-sandwich compounds of beryllium may serve as reasonable models for analogous compounds of transition metals and that their study may therefore provide useful interim information until suitable treatments for the latter are developed.

MNDO has been parametrized for hydrogen and the second row elements Be, B, C, N, O, and F[5,7] and, as yet without d AOs, for Cl.[8] Calculations for several hundred molecules of all kinds have given results in generally good agreement with experiment for heats of formation, molecular geometries, dipole moments, ionization energies, electron affinities,[9a] and molecular vibration frequencies.[9b] The energies calculated for beryllium compounds are less easily tested because of the lack of thermochemical data for these species in the gas phase. Other properties, however, agree with experiment, and the energies and geometries calculated by MNDO for smaller molecules containing beryllium are similar to those obtained by ab initio calculations.[7] Thus, the most stable forms of cyclopentadienylberyllium hydride and acetylide were correctly[10,11] predicted to involve bonding of the metal to the face of the ring, although σ-bonded isomers were calculated to be stable by MNDO and about 10 kcal/mol higher in energy.[7]

Regarding the accuracy and reliability of MNDO in general, an interesting indication is provided by reference to a recent paper by Halgren et al.[12] in which they compare a wide variety of procedures other than ours. For the group of reactions they use as a criterion, the average error in heats of formation calculated by MNDO is less than that given by any of the methods Halgren et al. considered, including an ab initio SCF–MO one using a basis set of double-ζ type. The average errors in the case of analogous minimum basis set procedures, or Lipscomb's PRDDO method, are three times greater than that from MNDO. In general, the errors in all molecular properties calculated by MNDO seem as a rule to be no greater than those given by ab initio methods using very large basis sets.[19]

Recently, the properties of mono- and dibenzocyclopentadienyl anions (indenyl, $C_9H_7^-$, and fluorenyl, $C_{13}H_9^-$, respectively) as ligands have attracted attention. The indenyl ligand normally forms complexes with transition-metal ions that have η^5 coordination,[13] although σ-bonded indenyl complexes (e.g., of mercury[14]) are known, and coordination to the six-membered ring of the 1-H protonated ligand has been observed.[15] Metal complexes of the fluorenyl ligand have recently been synthesized[16] and appear to be pentacoordinated,[16] although isomers with η^6 coordination have recently been reported (i.e., $Mn(\eta^6\text{-}C_{13}H_9)(CO)_3$[17a] or $Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_{13}H_9)$[17b]). In the case of the maganese complex, slow

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