Table I. Energy Transfer Data

donor	acceptor	λ_D[a]	λ_A[b]	K_{eq}(25 °C)	ΔH[c]	ΔS[d]
chrysene	naphthalene	580	420	1.1×10^{-3}	4.0 ± 0.1	0.04 ± 0.3
benzophenone	biphenyl	535	395	12.0	−2.0 ± 0.2	−1.8 ± 0.5
benzophenone	triphenylene	535	400	260	−2.1 ± 0.1	4.3 ± 0.4

[a] Wavelength (nm) where donor absorbance predominates. [b] Wavelength (nm) where acceptor absorbance predominates. [c] In kcal/mol. [d] In gibbs/mol.

changes resulting from excitation. Our results show that entropic terms can account for differences of over an order of magnitude in K_{eq}; further, the entropy changes observed can be interpreted in terms of the relative conformational freedom of the ground and excited states involved. The systems (solvent) examined are chrysene–naphthalene (toluene), benzophenone–biphenyl ($CF_3C_6H_5$), and benzophenone–triphenylene ($CF_3C_6H_5$). The measurements were carried out by using laser photolysis techniques[15] and the same analytical approach described by Kira and Thomas,[6] based on transient absorption measurements at two selected wavelengths where the excited donor and acceptor absorb preferentially. In order to establish that the equilibrium condition is met one obtains the ratio of the two traces at both wavelengths or calculates the equilibrium constant as a function of time; a time-independent value indicates that equilibrium has been achieved. Figure 1 illustrates a pair of traces and their ratio. The values of ΔS and ΔH can then be determined from a plot of log K_{eq} vs. T^{-1}, Figure 2. Table I summarizes the data. The enthalpy changes do not hold any significant surprises; in the case of naphthalene–chrysene the value of ΔH coincides with the spectroscopic energy difference,[6] and the other examples agree with reports already in the literature.[5,6] They will be discussed in detail in a full report. The equilibrium constant for the benzophenone–biphenyl system (12.0) is in reasonable agreement with values of 7 and 23 reported by Wagner[5] and Thomas.[6] For the benzophenone–triphenylene system, our value of 260 should be compared with the reported one of 133.[5]

It is noteworthy that the value of ΔS for the chrysene–naphthalene system is essentially zero, as one would expect for a pair of rigid molecules, where no significant changes in conformational freedom are expected upon excitation. On the other hand, in the benzophenone–triphenylene system $\Delta S = 4.3$ gibbs/mol; here, if we assume that triphenylene is essentially rigid, then the entropy of benzophenone must decrease by 4.3 gibbs/mol (apart from the multiplicity term) upon excitation, indicating a substantial decrease[16] in conformational freedom. Similarly, if we combine the last two entries in Table I, biphenyl must lose about 6.1 gibbs/mol upon excitation. It should be noted that these entropy differences refer to the relaxed triplet and ground state, rather than to the states involved in a "vertical" transition. We propose that this large entropy loss is the result of the freezing of the C–C bond between the biphenyl rings in a nearly planar conformation. Wagner[13b] has pointed out that "there exists a gross geometric difference between the ground state and the excited triplet state" of biphenyl. Interestingly, an entropy change of this magnitude will introduce a change of a factor of ca. 21 in an equilibrium constant.

We find the small value of ΔS in the benzophenone–biphenyl system rather surprising, since literature discussions of these molecules usually emphasize conformational effects in biphenyl, not in benzophenone. However, Kearns and Case[17] have observed a substantial separation between the O–O absorption and phosphorescence bands of benzophenone; further, the O–O phosphorescence band of aromatic ketones is known to be different for relaxed and unrelaxed triplets.[18]

Finally, it is interesting to consider a ΔS^* scale, of entropies of excitation, in much the same way in which we use triplet or singlet excitation energies. This could be useful in thermodynamic calculations, energy-transfer studies, and conformational effects in photochemistry. For example, the entropy effects observed for benzophenone and biphenyl provide a straightforward interpretation to the inefficiency of energy transfer in this system.[5] We are currently trying to measure sufficient examples to establish the basis for such a scale.

Acknowledgment. Thanks are due to S. E. Sugamori for technical assistance.

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(15) Details of our experimental setup have been reported elsewhere. Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747.

(16) Approximately equivalent to the loss of one internal rotation.

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Monomeric Tungsten(IV) Phenoxide and Thiolate Complexes

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To our knowledge there is no example in the literature of a complex of the type WX_4 where X is a monodentate anionic ligand.[1] We believe such 10e, d^2 species will be of interest in terms of their ability to bind and activate small molecules. The small molecule we are most interested in activating (using *two* such W(IV) centers) is molecular nitrogen. We now have firm evidence that $W^{IV}W_2(\mu\text{-}N_2)$ complexes can be prepared, either from W(VI) and hydrazine or directly from molecular nitrogen by reducing W(V).[2] It is thought that $W_2(\mu\text{-}N_2)$ complexes can be formed more easily than the more relevant $Mo_2(\mu\text{-}N_2)$ complexes owing to the expected greater reducing power of W(IV) vs. Mo(IV).

Blue, diamagnetic $W(DIPP)_4$ (DIPP = O-2,6-C_6H_3-*i*-Pr_2) can be prepared by heating $WCl_4(Et_2S)_2$ and 4 equiv of LiDIPP in a mixture of toluene and ether at 40 °C overnight.[3] An X-ray structural study[4] shows $W(DIPP)_4$ to be nearly square planar (Figure 1) with trans-O–W–O angles of 168° and cis angles of 90–91°. W–O–C angles vary from 154° to 159°. W–O bond lengths vary from 1.85 to 1.87 Å. The four phenyl ring systems

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(1) (a) $W(CH_2C_6H_5)_4$ appears to be well characterized[1b] although no structure has been reported. The benzyl ligand, however, may behave as a benzallyl ligand and therefore does not qualify as an unambiguously monodentate ligand. (b) Thiele, K. H.; Russek, A.; Opitz, R.; Mohai, B.; Brüser, W. *Z. Anorg. Allg. Chem.* **1975**, *412*, 11.

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(3) A solution of $WCl_4(Et_2S)_2$ (0.59 mmol, 0.300 g) in 3 mL of toluene at −30 °C was added to LiDIPP(ether) (2.37 mmol, 0.613 g) in 20 mL of ether at −30 °C. The mixture was stirred for 1.5 h at 25 °C then heated in a sealed vessel at 40 °C for 14 h. The precipitated salts were filtered off and the solvents removed in vacuo. The crude product was recrystallized from pentane to give dark blue crystals (0.25 g, 47%). Anal. Calcd for $WC_{48}H_{68}O_4$: C, 64.57; H, 7.68. Found: C, 64.48; H, 7.75.

(4) $W(DIPP)_4$ crystallizes in the space group $C2/c$ with $a = 30.557$ (5) Å, $b = 13.434$ (2) Å, $c = 22.312$ (3) Å, $\beta = 91.99$ (1)°, $V = 9153.6$ Å^3, $Z = 8$, ρ(calcd) = 1.296 g cm^{-3}, and $\mu = 24.23$ cm^{-1}. Data were collected at −50 °C on an Enraf-Nonius CAD4F-11 diffractometer by using Mo Kα radiation. A total of 8054 reflections ($\pm h$, $+k$, $+l$) were collected in the range $3° \leqslant 2\theta \leqslant 50°$ with the 5006 having $F_o > 6\sigma(F_o)$ being used in the structure refinement, which was by full-matrix least-squares techniques (241 variables) using SHELX-76. Final $R_1 = 0.042$ and $R_2 = 0.046$. An empirical absorption correction was applied.

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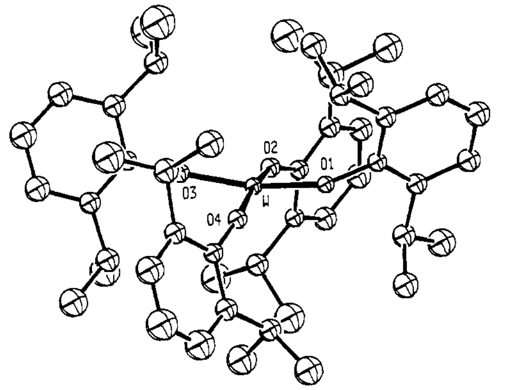

Figure 1. ORTEP diagram of $W[O\text{-}2,6\text{-}C_6H_3(CHMe_2)_2]_4$ (30% probability thermal ellipsoids).[4] Hydrogen atoms have been omitted for clarity.

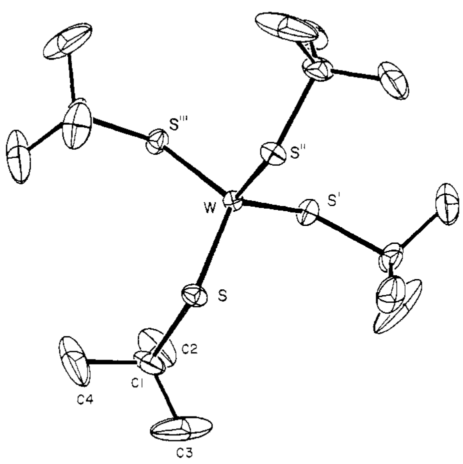

Figure 2. ORTEP diagram of $W(SCMe_3)_4$ (30% probability thermal ellipsoids).[13] Hydrogen atoms have been omitted for clarity.

are "stacked" around the perimeter so that the spaces above and below the WO_4 plane are filled by the eight isopropyl groups. The coordination sphere clearly is very crowded, as judged from a space-filling drawing of $W(DIPP)_4$ and the fact that $W(DIPP)_4$ does not react with 3-hexyne (cf. $W(2,6\text{-}DMP)_4$ below).

A similar reaction between $WCl_4(Et_2S)_2$ dissolved in toluene and 4 equiv of Li-2,6-DMP (2,6-DMP = $O\text{-}2,6\text{-}C_6H_3Me_2$) in THF yields red crystals of a diamagnetic product with the formula $W(2,6\text{-}DMP)_4$.[5] $W(2,6\text{-}DMP)_4$ is considerably more reactive than $W(DIPP)_4$. For example, it reacts immediately with 3-hexyne or phenylacetylene to form complexes with the formula $W(2,6\text{-}DMP)_4$(acetylene).[6] A preliminary X-ray study shows $W(2,6\text{-}DMP)_4$ to be a monomer with a nearly planar structure analogous to $W(DIPP)_4$. Therefore, we believe the core structure in $W(DIPP)_4$ and $W(2,6\text{-}DMP)_4$ is determined by electronic, rather than steric, factors, the exact nature of which remains to be determined.

Complexes of the type $W(\text{phenoxide})_4Cl_2$[7] can be prepared by adding WCl_6 to an excess of the phenol and heating the mixture to the melting point of the phenol [phenoxide = 2,6-DMP, 3,5-DMP, or TBP (*tert*-butyl *p*-phenoxide)].[8] Analogous complexes containing diisopropyl phenoxide could not be prepared. $W(2,6\text{-}DMP)_4Cl_2$ (1 g) can be reduced cleanly to $W(2,6\text{-}DMP)_4$ (2 h, 50% yield) by using sodium amalgam (0.5%) in diethyl ether (50 mL). An analogous reduction of $W(TBP)_4Cl_2$ in dimethoxyethane gave a red, crystalline complex with the empirical formula $W(TBP)_4$, but which does not react with 3-hexyne.[9] Even though the ^1H NMR spectrum shows only one type of TBP ligand on the NMR time scale down to −80 °C, we believe this complex is a dimer analogous to $[Mo(OCHMe_2)_4]_2$.[10] So far we have not been able to characterize the product(s) of the reduction of $W(3,5\text{-}DMP)_4Cl_2$. We believe that $W(3,5\text{-}DMP)_4$ may be prevented sterically from forming a dimer but may be able to form a $\mu\text{-}N_2$ complex with a TBP arrangement about each metal (cf. $[Ta(CHCMe_3)(CH_2CMe_3)(PMe_3)_2]_2(\mu\text{-}N_2)$[11]).

So far we have prepared one tetrathiolate complex. The reaction between $WCl_4(Et_2S)_2$ and 2-methylpropane-2-thiol at 0 °C in toluene in the presence of 4 equiv of triethylamine yields dark red crystalline $W(SCMe_3)_4$ in 30–40% yield.[12] An X-ray structural study[13] shows $W(SCMe_3)_4$ to be isomorphous and isostructural with $Mo(SCMe_3)_4$[14] with W–S = 2.236 (4) Å, S–C = 1.871 (18) Å, W–S–C = 119.5 (6)°, and three pairs of S–W–S angles of 94.3 (2)° (S,S''; S',S'''), 117.0 (2)° (S,S'''; S',S''), and 118.0 (2)° (S,S'; S'',S'''; Figure 2). Like $Mo(SCMe_3)_4$, $W(SCMe_3)_4$ does not appear to react cleanly with simple π-bonding ligands such as internal acetylenes. Therefore, we expect that we must employ sterically protected benzene thiolates, an approach that has been successful recently for preparing Mo(IV) thiolate complexes.[15]

Although none of the W(IV) complexes reported here appears capable of binding dinitrogen irreversibly in the form of a $W_2(\mu\text{-}N_2)$ complex, we still believe that this type of dinitrogen complex may be formed under the right circumstances. Work is continuing under this assumption.

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(5) A solution of $WCl_4(Et_2S)_2$ (0.988 mmol, 0.500 g) in ~40 mL of toluene that had been cooled to −30 °C was added rapidly to a solution of $Li(O\text{-}2,6\text{-}Me_2C_6H_3)$ (3.95 mmol, 0.506 g) in 5 mL of THF that also had been cooled to −30 °C. After 1 h ~45 mL of pentane was added, the solution was filtered through Celite, and the solvents were removed in vacuo. The dark red, oily residue was dissolved in a minimum amount of toluene, and 5 volumes of pentane were added. The solution was filtered to remove some amorphous tan solids. The solvents were removed in vacuo to afford the crude product as a dark red, sticky solid in a yield of ~75% by integration vs. an internal standard. The product may be recrystallized with difficulty from toluene/pentane (0.200 g, 30%) or from ether as dark red blocks. Anal. Calcd for $WC_{32}H_{36}O_4$: C, 57.50; H, 5.43. Found: C 57.00; H, 5.52.

(6) An equimolar quantity of 3-hexyne was added to $W(2,6\text{-}DMP)_4$ in ether to give a bright red solution from which $W(2,6\text{-}DMP)_4$(3-hexyne) can be isolated in ~50% yield as red-orange flakes. At 25 °C all phenoxides and the two ends of the acetylene are equivalent on the NMR time scale. The acetylenic carbon atom signal is found at 207.1 ppm (CD_2Cl_2) in the ^{13}C NMR spectrum.

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(8) $W(2,6\text{-}DMP)_4Cl_2$ must be prepared from WCl_6 and 10 equiv of the phenol at a temperature where the phenol melts. The other compounds can be prepared from WCl_6 and 4 equiv of the phenol in CCl_4 (1 h reflux). The pentane-insoluble brown complexes have the trans geometry according to their NMR spectra.

(9) Anal. Calcd for $WC_{40}H_{52}O_4$: C, 61.54; H, 6.71. Found: C, 61.42; H, 6.51.

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(12) A solution of triethylamine (3.95 mmol, 551 μL) and $WCl_4(Et_2S)_2$ (0.988 mmol, 0.500 g) in 25 mL of toluene was cooled to 0 °C and 2-methylpropane-2-thiol (3.95 mmol, 446 μL) in 5 mL of toluene was added dropwise over a few minutes with stirring. The solution turned deep red and tan solids precipitated. After stirring for ~15 min at room temperature the solution was filtered, the solvents were removed in vacuo, and the residue was extracted with pentane. The extract was filtered to remove some black solids. Cooling the pentane solution yielded 0.205 g (38%) of red-black needles.

(13) Data were collected at −65 °C. A total of 1297 reflections $(+h, +k, +l)$ were collected in the range $3° \leq 2\theta \leq 50°$ with the 921 having $F_o > 4\sigma(F_o)$ being used in the structure refinement by full-matrix least-squares techniques (49 variables, SHELX-76). Final $R_1 = 0.063$ and $R_2 = 0.085$. All non-hydrogen atoms were refined anisotropically. Space group $P4_22_12$, $a = b = 10.912$ (2) Å, $c = 10.163$ (2) Å, $V = 1210.1$ Å^3, $Z = 2$, ρ(calcd) = 1.483 g cm^{-3}, $\mu = 93.8$ cm^{-1}. An empirical absorption correction was applied. The molecule possesses crystallographically imposed 222 symmetry. The S' ligand is at $-x,-y,z$, S'' at $y,x,-z$, and S''' at $-y,-x,-z$.

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