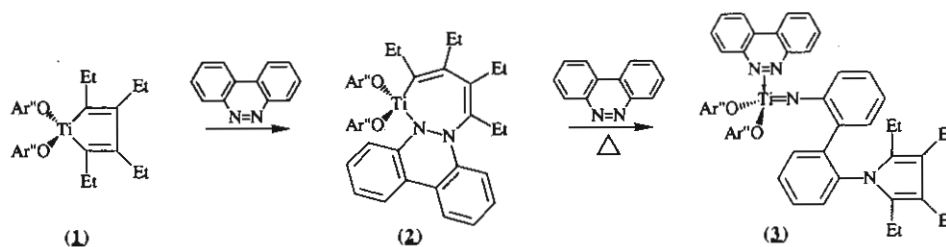


Scheme 1



Ar'O=2,6-Diphenylphenoxide

[(Ar'O)₂Ti(NPh)(1,10-phenyl)]₃, respectively.^{4,9} The bonding of the benzo[*c*]cinnoline ligand in **3** is also worthy of note. A number of group 4 metal η²-azobenzene complexes are now known.¹⁰⁻¹² However, the azobenzene molecule is typically η²-N,N bound to a formally d², M²⁺ metal center. Structural studies show the resulting molecules to be better described as containing diazametallacyclopropane rings, with short M-N and long N-N distances. In compound **3** the diazo unit is bound to a d⁰ metal center with no prospects for any back-bonding from the metal into the π* orbital of the N=N unit. The N-N distance of 1.284 (6) Å found in **3** is very close to the distance of 1.253 (3) Å found for uncoordinated azobenzene.¹³ This distance is much shorter than the distances of 1.416 (8) and 1.42 (1) Å found for the two independent molecules in [(Ar'O)₂Ti(PhNNPh)(py)₂],¹⁰ 1.339 Å in Cp₂Ti(η²-PhNNPh),¹² and 1.434 (4) Å for Cp₂Zr(η²-PhNNPh)(py).¹¹ The Ti-N(diazo) distances in **3**, 2.175 (5) and 2.125 (5) Å, are much longer than the values of 1.949 (6) and 1.963 (6) Å in [(Ar'O)₂Ti(η²-PhNNPh)(py)₂].¹⁰ These latter distances are comparable to those expected for titanium-amido bonding, while the long distances in **3** are closer to simple dative bond distances.¹⁴ Hence, the benzo[*c*]cinnoline molecule in aryl-imido **3** represents a diazo ligand that is purely σ-bound to titanium with no evidence for metal to ligand π-back-bonding.

Experimental Section

Preparation of Ti(OAr')₂(C₄Et₄-C₆H₄N-NC₆H₄) (2). To a benzene solution of Ti(OAr')₂(C₄Et₄) (**1**) (0.25 g, 0.36 mmol) was added 1 equiv of benzo[*c*]cinnoline (0.07 g, 0.36 mmol). The mixture was stirred for 1 h at room temperature; then the solvent was removed under vacuum. The resulting residue was redissolved in a minimum of fresh benzene and layered with hexane to induce formation of light yellow crystals of product. The crystals were washed with hexane and dried under vacuum. Anal. Calcd for TiC₆₀H₅₄N₂O₂ (**2**): C, 81.61; H, 6.16; N, 3.17. Found: C, 81.25; H, 6.56; N, 3.15. ¹H NMR (C₆D₆, 30 °C), δ: 6.50-7.87 (m, aromatics); 5.42 (dd, ortho proton on C₆H₇N-NC₆H₇); 2.71 (sextet), 1.73-2.10 (m, CH₂CH₃); 1.03 (t), 0.86 (t), 0.73 (t), 0.35 (t, CH₂CH₃). Selected ¹³C NMR data (C₆D₆, 30 °C), δ: 210.7 (Ti-C); 160.7, 159.7 (Ti-O-C); 28.0, 23.3, 22.9, 20.7 (CH₂CH₃); 15.4, 15.1, 14.8, 13.8 (C-H₂CH₃).

Preparation of Ti(OAr')₂(=NC₆H₄-C₆H₄NC₆Et₄) (3). A benzene solution of Ti(OAr')₂(C₄Et₄) (**1**) (0.25 g, 0.36 mmol) and 2 equiv of benzo[*c*]cinnoline (0.14 g, 0.72 mmol) was heated at 100 °C for 2 h. The solvent was then removed under vacuum, and the resulting residue was redissolved in a minimum of fresh benzene. The benzene solution was layered with hexane to induce formation of very dark yellow crystals of products that were suitable for X-ray diffraction. The crystals were washed with hexane and dried under vacuum. Anal. Calcd for TiC₇₂H₆₄N₄O₂ (**3**): C, 81.18; H, 6.06; N, 5.26. Found: C, 81.40; H, 6.36;

N, 4.82. ¹H NMR (C₆D₆, 30 °C), δ: 5.08-7.80 (m, aromatics); 2.14 (q), 2.16 (m, CH₂CH₃); 1.13 (t), 0.77 (t, CH₂CH₃). Selected ¹³C NMR data (C₆D₆, 30 °C), δ: 18.5, 18.2 (CH₂CH₃); 17.4, 16.3 (CH₂CH₃).

Acknowledgment. We thank the National Science Foundation (Grant CHE-8915573) for support of this research.

Supplementary Material Available: A fully labeled ORTEP drawing of **3**, a textual presentation of the details of the crystallographic study, and tables of crystal data, fractional coordinates, temperature factors, and bond distances and angles (24 pages); a listing of observed and calculated structure factors (26 pages). Ordering information is given on any current masthead page.

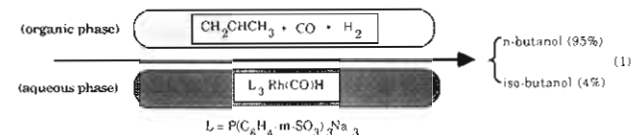
Contribution from the Department of Chemistry,
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Water-Soluble Organometallic Compounds. 1. Synthesis, Characterization, and X-ray Structure of [Na-kryptofix-221]₃[W(CO)₅P(C₆H₄-*m*-SO₃)₃]

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and Joseph H. Reibenspies

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The interest in water-soluble organometallic complexes has increased dramatically since the development of the Rhone-Poulenc/Ruhrchemie biphasic catalysis process.^{1,2} This procedure, which utilizes a water-soluble rhodium catalyst containing the TPPTS (trisodium tris(*m*-sulfonatophenyl)phosphine) ligand, is capable of performing the hydroformylation process outlined in eq 1. Other similar water-based organometallic catalysts have



been employed for a variety of important chemical processes.³ On spectroscopic evidence, it is generally felt with regard to the M-P bond that electronically the sulfonated phosphine is quite similar to that of its non-sulfonated analogue PPh₃. Nevertheless, the two ligands should differ significantly in their steric influence. In addition, when the metal center is multiply substituted with

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TPPTS ligands, the possibility exists for interligand interactions that can greatly affect the reactivity of such complexes.⁴

We have begun comparative reactivity and structural studies of complexes containing the TPPTS ligand and its PPh₃ counterpart. In this report the structural characterization of a complex containing the TPPTS ligand is presented for the first time, although the structure of a monosulfonated phosphine complex of palladium has recently been elucidated.⁵

Experimental Section

Reagents. Methanol purchased from Fisher (spectrophotometric grade) was dried by distillation over Mg and I₂ under a N₂ atmosphere. Tetrahydrofuran was purchased from Fisher and purified over sodium benzophenone ketyl under a nitrogen atmosphere. Water was triply distilled, deionized, and degassed with N₂. Tungsten hexacarbonyl, 2-methoxyethanol, kryptofix-221 (4,7,13,16,21-penta-oxa-1,10-diazabicyclo[8.8.5]tricosane), TPPTS (trisodium tris(*m*-sulfonatophenyl)phosphine), and carbon monoxide were obtained from Strem Chemical Co., Aldrich Chemical Co., EM Science, Exxon Corporate Research, and Airco Inc., respectively. All chemicals were used without further purification.

Instrumentation. IR spectra were collected on either an IBM 85 or a Mattson 6020 spectrometer. Aqueous infrared spectra were taken by employing a CIRCLE (cylindrical internal reflectance) cell, furnished by Spectra Tech Inc. Other infrared spectra in methanol and 2-methoxyethanol were taken with both the CIRCLE and standard 0.1-mm CaF₂ solution cells. Kinetics measurements were taken by using a Reactor Cell, furnished by Spectra Tech Inc. NMR spectra were collected with both Varian XL-200 (for ¹³C and ¹H) and Varian XL-200E (³¹P) spectrometers. X-ray structure analysis was performed on a Nicolet R3m/V diffractometer employing Nicolet SHELXTL-PLUS on a Microvax II computer. All manipulations were performed by using a Vac Atmospheres glovebox or a nitrogen/vacuum Schlenk line.

Preparation of Na₃[W(CO)₅P(C₆H₄-*m*-SO₃)₃] (1). A solution of W(CO)₆ was prepared by dissolving 0.654 g (0.002 mol) in 75 mL of MeOH. This solution was placed in a photolysis vessel and irradiated with a 400-W UV lamp for 30 min to yield the very substitutionally labile W(CO)₅MeOH species, as identified by IR spectroscopy ($\nu(\text{CO})$ 2075 w, 1932 s, and 1887 m cm⁻¹). The methanol adduct was added by cannula to a flask containing 1 equiv (1.06 g, 0.002 mol) of the solid TPPTS ligand. The reaction was monitored by the disappearance of the $\nu(\text{CO})$ infrared bands associated with the methanol adduct, with concomitant appearance of $\nu(\text{CO})$ bands due to W(CO)₅TPPTS (1). 1 was filtered through Celite and precipitated by the addition of isopropyl alcohol to yield a very flocculent pale yellow solid. The solid was centrifuged and the supernatant liquid decanted to yield a wet yellow paste. Final drying of the compound was accomplished under vacuum at ambient temperature over a 24-h period.

Preparation of [Na-kryptofix-221]₃[W(CO)₅P(C₆H₄-*m*-SO₃)₃] (2). [Na-kryptofix-221]₃[W(CO)₅P(C₆H₄-*m*-SO₃)₃] was synthesized by initially making a slurry of 1 in 25 mL of THF, followed by the slow addition of 2-methoxyethanol (7 mL) until the solid was completely dissolved and the solution appeared clear. A 3-equiv amount of kryptofix-221 (0.59 g) dissolved in acetonitrile (5 mL) was added to the solution, which was allowed to stir for 24 h. The resultant solution was filtered and transferred to a very large Schlenk tube containing an open test tube of diethyl ether. Slow diffusion of the solvents resulted in the formation of bright yellow block-shaped crystals of 2 over a 3-week period.

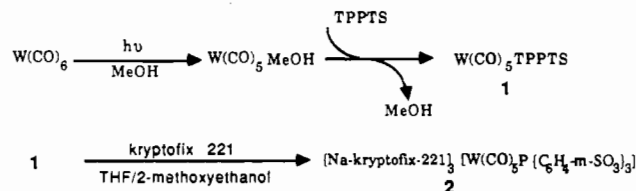
X-ray Crystal Structure Determination. A bright yellow block (0.18 mm × 0.20 mm × 0.22 mm) crystal was mounted on a glass fiber with epoxy cement, at room temperature, and cooled to 193 K in a nitrogen cold stream (Nicolet LT-2). Data collection was performed on a Nicolet R3m/V X-ray diffractometer in the range of 4.0° ≤ 2θ ≤ 55.0°. Lorentz and polarization corrections were applied to a total of 7621 reflections collected, of which 5598 were unique with *I* ≥ 4.0σ(*I*). The structure was solved by using direct methods (SHELXS, SHELXTL-PLUS program package of Sheldrick). All pertinent crystallographic information is listed in Table I.

Rate Measurements. The reaction involving the displacement of the TPPTS ligand from the tungsten metal center was followed by IR spectroscopy. Initially 0.150 g of 1 was dissolved in 15 mL of a mixture of THF/H₂O (1:1 by volume) in a small flask. This solution was then cannulated into a Reactor Cell, which was then pressurized with 400 psi of CO. The temperature was then ramped to some temperature between

Table I

formula	C ₇₁ H ₁₀₈ N ₆ O ₂₉ Na ₃ PS ₃ W	fw	1889.6
<i>a</i>	12.591 (4) Å	space group	P1 (No. 1)
<i>b</i>	13.260 (4) Å	<i>T</i>	193 K
<i>c</i>	13.318 (4) Å	λ(Mo Kα)	0.71073 Å
α	102.45 (2)°	ρ _{calc}	1.485 g cm ⁻³
β	100.31 (2)°	μ	1.57 mm ⁻¹
γ	95.79 (2)°	<i>T</i> _{max}	0.9623
<i>V</i>	2113.6 (11) Å ³	<i>T</i> _{min}	0.8513
<i>Z</i>	1	<i>R</i>	0.086
no. of rflns colld	7621	<i>R</i> _w	0.099
no. of unique rflns	5598	<i>S</i>	6.14

Scheme I



115 and 145 °C, and IR data were collected every 150 s.

Results and Discussion

The title compound was synthesized according to Scheme I under a nitrogen atmosphere by employing Schlenk techniques. W(CO)₆ was photolyzed in MeOH to yield the W(CO)₅MeOH species, which in turn was added to a flask containing the TPPTS ligand to yield 1. The solution was filtered, and 1 was precipitated by the addition of isopropyl alcohol to yield a yellow solid. Crystals of 2 were obtained by first making a slurry of 1 in THF, followed by addition of 2-methoxyethanol until the solid was completely dissolved. Kryptofix-221 was added to the solution, which was then allowed to stir for 24 h. Slow diffusion of the diethyl ether resulted in the formation of bright yellow block-shaped crystals of 2 over a 3-week period. All attempts to grow crystals of 1 without the encapsulation of the Na⁺ via kryptofix-221 were unsuccessful.⁶

Both complexes 1 and 2 are extremely soluble in water and 2-methoxyethanol, slightly soluble in methanol, and almost completely insoluble in less polar solvents. Infrared spectra for complexes 1 and 2 were determined in water, while the spectrum for the W(CO)₅PPh₃ analogy was observed in THF. Little difference is seen in the $\nu(\text{CO})$ region for all three complexes, as noted in Table II. Included in Table II for comparison are the ¹³C and ³¹P chemical shifts for the TPPTS and PPh₃ derivatives, which also display a great deal of similarity.

The compound [Na-kryptofix-221]₃[W(CO)₅P(C₆H₄-*m*-SO₃)₃] has been characterized by single-crystal X-ray diffraction. Table I lists all crystallographic data of interest. The structure of 2 consists of an array of the four discrete ionic units at normal van der Waals distances (Figure 1). The three-dimensional structure of one of the cations is shown in Figure 2, which illustrates that the sodium ion is heptacoordinated, analogous to the original structural report.⁷ The closest Na⁺...O₃S distance is 5.47 Å; hence, there is no sodium cation interaction with groups outside of the kryptofix cage. The disposition of the ligands about the tungsten atom in the anion is that of a regular octahedron, where the average C_{ax}-W-C_{eq} angle is 89.6 (19)° (Figure 3). The trisulfonated phosphine ligand is situated 2.554 (11) Å from the tungsten metal center, a distance seen for related W-P bonds.⁸⁻¹²

(6) Attempts at crystallizing the unencapsulated Na salt of complex 1 by supersaturation, mixed solvents, and solvent diffusion failed. Ion-exchange reactions were performed to provide the Ca, Ba, Sr, K, Rb, and Cs salts, which also did not lead to crystalline solids.

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Table II^a

	IR			NMR			
	$\nu(\text{CO}), \text{cm}^{-1}$			δ, ppm	$J(^{31}\text{P}-^{13}\text{C}), \text{Hz}$	δ, ppm	$J(^{183}\text{W}-^{31}\text{P}), \text{Hz}$
1	2073 w	1946 s	1932 m sh	196.7 (cis) 199.6 (trans)	6.7 20.0	26.9	247.7
1a	2075 w	1946 s	1938 m sh				
2	2073 w	1943 s	1938 m sh				
3	2069 w	1939 s	1930 m sh	198.0 (cis) 199.8 (trans)	7.0 22.0	21.2 (20.6) ^c	243.7

^aThe complexes are listed with the following corresponding infrared and NMR solvents, respectively: $\text{W}(\text{CO})_5\text{TPPTS}$ (1), H_2O , D_2O ; $\text{W}(\text{CO})_5\text{TPPTS}$ (1a), MeOH ; $[\text{Na-kryptofix-221}]_3[\text{W}(\text{CO})_5\text{P}(\text{C}_6\text{H}_4\text{-}m\text{-SO}_3)_3]$ (2), H_2O ; $\text{W}(\text{CO})_5\text{PPh}_3$ (3), THF , CDCl_3 . ^bThe free ligands' ^{31}P chemical shifts for TPPTS in water and PPh_3 in CDCl_3 are -5.48 and -5.21 ppm, respectively. ^cGrim, S. O.; Wheatland, D.A.; McFarlane, W. *J. Am. Chem. Soc.* 1967, 89, 5573. Included in this paper are the ^{31}P chemical shifts for a wide range of phosphine-substituted tungsten pentacarbonyl complexes.

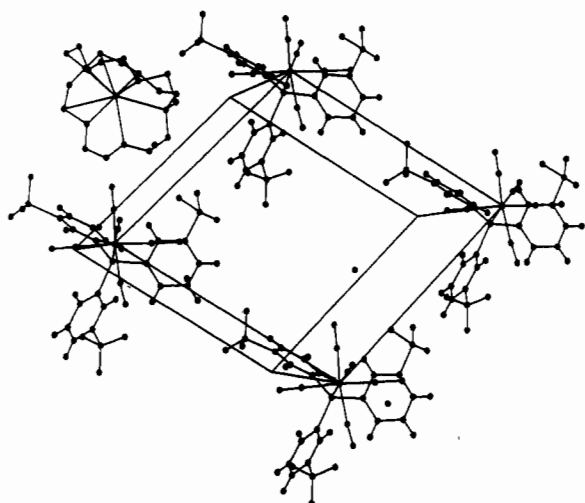


Figure 1. Ball and stick representation of 2, showing the arrangement of the cryptated Na cations with respect to the metal anions. The cryptates for all but one of the Na-kryptofix-221 cations have been omitted for clarity.

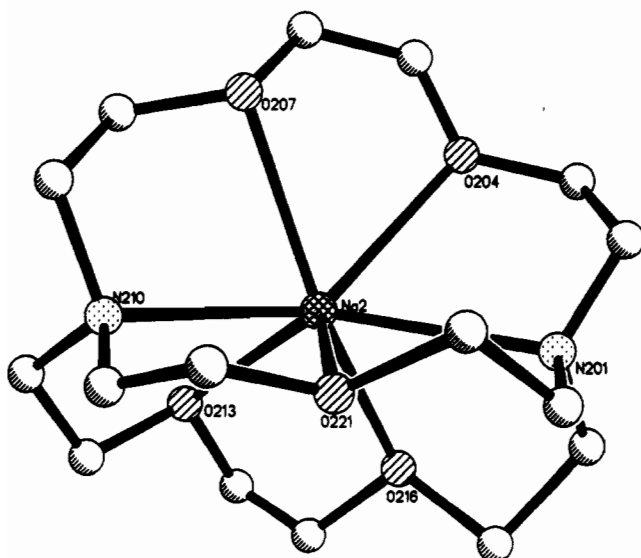


Figure 2. Ball and stick representation for one of the Na-kryptofix-221 cations.

Of importance is the relative steric influence of the trisulfonated phosphine ligand to that of PPh_3 . On the basis of a molecular model from the structure data, it appears to be approximately 20% larger than PPh_3 ,¹³ or in terms of Tolman's cone angle,¹⁴ a value

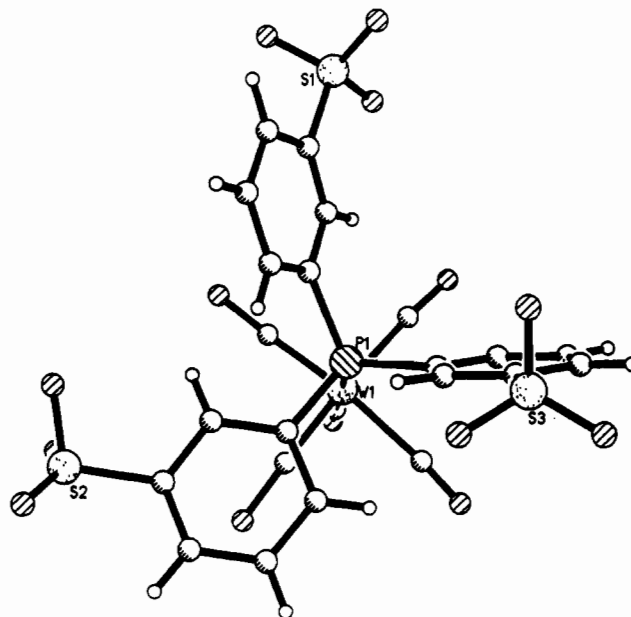


Figure 3. Ball and stick representation for the $[\text{W}(\text{CO})_5\text{P}(\text{C}_6\text{H}_4\text{-}m\text{-SO}_3)_3]^{2-}$ anion, illustrating the steric bulk of the TPPTS ligand.

of 170° would be appropriate. Nevertheless, we have been successful in synthesizing the *cis*- $\text{W}(\text{CO})_4(\text{TPPTS})_2$ derivative and hope to evaluate interligand interactions with this species.¹⁵ Indeed, it may be interligand interactions by way of the Na^+ ions that facilitate the exclusive isolation of the *cis* isomer in this instance.¹⁶

Thus far, our investigations have revealed a great deal of similarity in the relevant structural and spectroscopic parameters for complexes 1 and 2 and their PPh_3 analogue, complex 3. Experiments in progress are designed to compare the activation parameters for W-P bond dissociation in 1 and 3. The dissociative rate constant (k_1) for TPPTS loss in $\text{W}(\text{CO})_5(\text{TPPTS})$ with concomitant formation of $\text{W}(\text{CO})_6$ carried out in a 1:1 mixture by volume of THF/water at 130°C under 400 psi of CO pressure has been determined to be $1.14 \times 10^{-4} \text{ s}^{-1}$.¹⁷ Hence, the calculated free energy of activation for W-P bond dissociation in 1 is 31.6

- (13) Steric influences of phosphine ligands in 2 and selected metal pentacarbonyl phosphines were measured on the basis of angles calculated from crystallographic data for M-P-X geometries, where X represents the atom of the phosphine ligand giving the greatest angle.
- (14) Tolman, C. A. *Chem. Rev.* 1977, 77, 313.
- (15) This derivative has been prepared from either *cis*- $\text{W}(\text{CO})_4(\text{MeOH})_2$ or *cis*- $\text{W}(\text{CO})_4(\text{THF})_2$ and has been partially characterized by infrared spectroscopy.
- (16) For example, an analogous reaction of *cis*- $\text{W}(\text{CO})_4(\text{THF})_2$ with $\text{P}(\text{C}_6\text{H}_4\text{-}m\text{-CH}_3)_3$ yields a mixture of *cis*- and *trans*- $\text{W}(\text{CO})_4[\text{P}(\text{C}_6\text{H}_4\text{-}m\text{-CH}_3)_3]_2$, with the latter isomer being in greater yield (unpublished observations of L. Bates in our laboratories).
- (17) These reactions were carried out in a stainless steel in situ high-pressure CIR reactor cell on an IBM 85 FTIR spectrometer. A high pressure of CO is required to avoid complication from the back-reaction.

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kcal/mol, a value in good agreement with those found for comparable processes involving the triphenylphosphine ligand.¹⁸

Acknowledgements. Financial support from the National Science Foundation (Grant 88-17873) and the Robert A. Welch Foundation is gratefully acknowledged.

Supplementary Material Available: Text describing X-ray procedures and tables listing refinement parameters, atomic coordinates, isotropic thermal parameters, anisotropic thermal parameters, H atom coordinates and isotropic displacement parameters, and all bond distances and bond angles (18 pages); a listing of observed and calculated structure factors (27 pages). Ordering information is given on any current masthead page.

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Reaction Enthalpies of Atom Transfer to Electronically Excited Tetrakis(pyrophosphito)diplatinate(II)

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The photochemistry of d^8-d^8 binuclear complexes (M_2 ; $M = \text{Pt, Rh, Ir}$) has been an extremely active area of research.¹ These complexes possess $d\sigma^*p\sigma$ triplet states (M_2^*) that are sufficiently long-lived to undergo bimolecular reactions, such as electron and atom transfer.¹⁻³ In particular, excited-state atom transfer of these complexes can be an important step in catalytic photo-reactions.¹ For example, the tetrakis(pyrophosphito)diplatinate(II) complex, $\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4^{4-}$, catalyzes the photochemical conversion of isopropyl alcohol into hydrogen and acetone.⁴

Although the kinetic behavior of the excited states of these binuclear complexes toward atom and electron transfer has been examined,¹⁻³ little is known about the thermochemistry of such processes. Herein, we report on the reaction enthalpies of hydrogen and halogen transfer to the excited and ground states of $\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4^{4-}$ (Pt_2). These enthalpies are useful in understanding the atom-transfer reactivity of the excited state of Pt_2 and comparing it to other reactive transition-metal complexes and radicals.

Experimental Section

Materials. $(n\text{-Bu}_4\text{N})_4[\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4]$ was prepared from the potassium salt as described previously.⁵ Methanol, CCl_4 , and benzene were obtained from J. T. Baker Inc. and used as received. Iodobenzene, benzyl alcohol, isopropyl bromide, and *tert*-butyl bromide were obtained from Aldrich and distilled before use. 2-Hydroxybenzophenone (Aldrich) was recrystallized.

Photoacoustic Calorimetry. The PAC experiment has been previously described.⁶ Photoexcitation was conducted at 365 nm (78.4 kcal/mol)

Table I. Experimental PAC Heats of Reaction and Calculated Bond Dissociation Energies of $\text{Pt}_2\text{X}^{\alpha\alpha}$

RX	$k_q, \text{M}^{-1} \text{s}^{-1} d$	$\Delta H_1 + \Delta H_2$	ΔH_2	$D_0(\text{RX})^e$	$D_0(\text{Pt}_2\text{X})$
$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ (1.5 M)	2.5×10^6	32.9 (4.7) ^f	-23.6	81.2 (1.5)	48.3 (4.9)
$(\text{C}_4\text{H}_9)_3\text{SnH}$ (0.2 M) ^g	1.2×10^7	28.2 (1.8)	-28.3	74.0 (2.0)	45.8 (2.7)
CCl_4 (0.05 M)	2.0×10^9	23.5 (1.6)	-33.0	73.1 (1.8)	49.6 (2.4)
$(\text{CH}_3)_3\text{CBr}$ (0.05 M)	$>10^9$	36.9 (1.3)	-19.6	67.3 (1.7)	31.3 (2.1)
$(\text{CH}_3)_2\text{CHBr}$ (10.6 M)	$1.7 \times 10^8 h$	35.3 (3.9)	-21.2	68.4 (1.2)	33.1 (4.1)
$\text{C}_6\text{H}_5\text{I}$ (0.063 M) ⁱ	1.6×10^9	31.4 (3.5)	-25.1	65.4 (2.0)	34.0 (4.0)

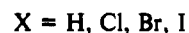
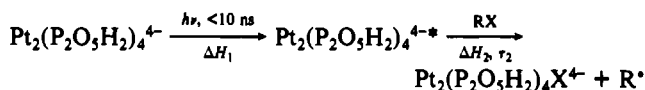
^a In CH_3OH with added substrate RX, at 298 °C. ^b Values are the average of at least five measurements. ^c ΔH and D_0 values in kcal/mol. ^d Values from refs 2 and 3. ^e Values from ref 11. ^f Errors in parentheses are $\pm 1\sigma$. ^g In 1:1 $\text{CH}_3\text{OH}/\text{benzene}$. ^h Value for $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{Br}$. ⁱ See ref 12.

by a nitrogen-pumped dye laser on argon-degassed samples at room temperature. The acoustic waves were detected by a PZT transducer (~ 0.5 MHz). The signal was amplified (Panametrics preamp, Model 5676), digitized (LeCroy 9400), and transferred to a laboratory computer for data analysis. The wave forms were the average of 60–80 laser pulses ($< 20 \mu\text{J}$). The transducer response function was obtained from photoexcitation of 2-hydroxybenzophenone. The optical densities of the calibration and sample compounds were ~ 0.8 and were adjusted to be within 1% of each other. Sample absorbances did not change significantly during the experiment. The time resolution of the transducer is approximately 10 ns–5 μs . Heat depositions that occur faster than 10 ns will not be differentiated, whereas those slower than 5 μs will not be detected.

Under reaction conditions where only one heat deposition was observed, $\Delta H = (1 - \alpha)E_{hr}$, where E_{hr} is the incident laser energy and α is the fraction of the incident photon energy released as heat. In the described experiments, $\Delta H = \Delta H_1$ in the absence of substrate RX and $\Delta H = \Delta H_1 + \Delta H_2$ in the presence of substrate RX. Under reaction conditions where two heat depositions were observed, $\Delta H_a = (1 - \alpha_a)E_{hr}$ and $\Delta H_b = -\alpha_b E_{hr}$, where α_a and α_b are the fractions of the incident photon energy released as heat in the depositions. The experimental enthalpic, α_a and α_b , and kinetic, $\tau_a \leq 10$ ns and τ_b , values were determined by deconvolution of the first 400 points of the acoustic wave forms.⁶ In the experiments where $10 \mu\text{s} \geq 1/(k_q[\text{RX}]) \geq 10$ ns, $\Delta H_a = \Delta H_1$ and $\Delta H_b = \Delta H_2$.

Results and Discussion

Photoexcitation (365 nm) of $\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4^{4-}$ (Pt_2) produces the triplet ($^3A_{2u}$) excited state $\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4^{4-*}$ (Pt_2^*) with unit efficiency.^{2,3} This highly reactive, long-lived ($\sim 10 \mu\text{s}$) state undergoes hydrogen and halogen atom transfer reactions with substrates, RX, to yield the radicals $\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4\text{X}^{\alpha}$ (Pt_2X) and R^{\bullet} , shown as follows:



The triplet state Pt_2^* and the radicals Pt_2X have been identified and characterized by transient absorption, resonance Raman, and infrared spectroscopies.^{2,3} In addition, the bimolecular rate constants, k_q , for the hydrogen and halogen atom transfer reactions with various substrates RX have also been measured. The radicals Pt_2X are also long-lived ($\geq 10 \mu\text{s}$) under the flash photolysis conditions and either disproportionate, atom-abtract from RX, or couple with R^{\bullet} .

The heats of these atom-transfer reaction reactions are determined by time-resolved photoacoustic calorimetry (PAC). PAC measures the volume changes of the system that result primarily from the thermal expansion of the solvent following photoexci-

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