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Large-Scale Syntheses of Several Synthons to the Dearomatization Agent $\{TpW(NO)(PMe_3)\}$ and Convenient Spectroscopic Tools for Product Analysis

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Summary: A series of complexes of the form $TpW(NO)(PMe_3)$-(η^2-arene) (where arene = benzene, anisole, dimethoxybenzene, trifluorotoluene, and naphthalene) are evaluated as practical synthons for the versatile dearomatization agent $\{TpW(NO)(PMe_3)\}$, considering air stability, synthetic scalability, and substitution lability. Large-scale syntheses (9−30 g) are reported for several of these complexes as well as their precursors ($TpW(NO)(CO_2)$, $TpW(NO)Br_2$, and $TpW(NO)(PMe_3)Br$), and methods for spectroscopic characterization of composition and stereochemistry for the arene complexes (including J_{PW} correlations) are summarized.

The coordination of an aromatic molecule to a d^6 transition metal complex profoundly affects its chemical nature. By adjusting the type of binding and electronic properties of the metal, widely differing chemical properties may be realized. Whereas conventional hexahapto-coordination of arenes by 12e$^-$ complexes such as $\{Cr(CO)_3\}$, $\{Mo(CO)_3\}$, $\{Mn(CO)_3\}^+$, $\{FeCp\}^+$, and $\{RuCp\}^+$ activates the aromatic toward nucleophilic addition, substitution, and deprotonation,[1,2] 14e$^-$ fragments such as $\{Mn(CO)_3\}^-$ [3,4] and 16e$^-$ complexes such as $\{Os(NH_3)_5\}^{2+}$, $\{TpRe(CO)(MeIm)\}$, $\{TpMo(NO)(MeIm)\}$, and $\{TpW(NO)(PMe_3)\}$ facilitate reactions with acids and electrophiles.[5] Of this latter group, the fragment $\{TpW(NO)(PMe_3)\}$ may prove to be the most versatile.[6,7] This most powerful π-base binds an exceptionally wide range of aromatic molecules from simple benzenes to polycyclic hydrocarbons and heterocycles.[7,8] Given the potential of this system and its predecessors to provide novel organic compounds,[7−9] we thought it would be useful to explore different routes to the intermediate $\{TpW(NO)(PMe_3)\}$, as well as to develop a set of spectroscopic tools to assist in identifying the chemical nature and stereochemistry of the associated complexes.

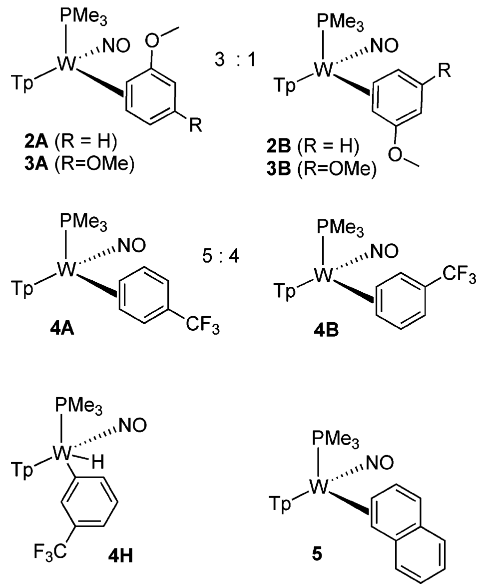

Figure 1. η^2-Arene complexes (**2**−**5**) and the oxidative addition product **4H**.

Synthons for $\{TpW(NO)(PMe_3)\}$. In exploring useful synthons to $TpW(NO)(PMe_3)(L)$ complexes, we considered the price of reagents, yield and scale of preparation, and air and thermal stability. We sought a complex of the form $TpW(NO)(PMe_3)(Y)$, where displacement of Y is facile at ambient temperature. Electrochemical studies of various complexes of this type[8−11] indicate that for any Y regarded as primarily a σ-donor (e.g., amine, halide, water, phosphine) the corresponding complex will have a reduction potential far too negative to be viable for short periods of time in air. On the other hand, alkenes and alkynes form complexes that are far too stable to be useful as synthons.[9,12] Thus, from an inital screen that included ketones, amides, alkenes, and arenes, we eventually settled on four arenes. The complexes (Y = benzene, **1**;[7] anisole,

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Table 1.

ligand	yield	half-life (solid; air)[b]	half-life (h)[b] (soln, air sat.)	half-life (h (°C)) (*substitution*, N_2)
benzene	8.66 g (50%) 15.1 g (40%)	2.3 h	0.7 (HPh)	1.1 (22)
anisole	10.0 g (44%)	3.0 h	0.7 ($CHCl_3$)	3.7 (22)
1,3-DMB[c]	6.5 g (41%)		1.0 ($CHCl_3$)	4.3 (22)
trifluorotoluene	30.4 g (55%)	~4 d	2.7 (CF_3Ph)	192 (22) 2 (50)
naphthalene	0.48 g (42%)	13 d	8.4 ($CHCl_3$)	220 (78)
[1,3-DMBH] (OTf)	8.9 g (43%)	41 d	7.7 (acetone)	86 (22)[a]

[a] Unknown decomposition product. [b] 22 °C. [c] DMB = 1,3-dimethoxybenzene.

Table 2.

ligand	ν(NO) (cm^{-1})	$E_{p,a}$ (V, NHE)	M−C−*H* (δ)	^{31}P (δ) (PMe_3)	$J_{W,P}$ (Hz)	$J_{P,H}$ (Hz) (M−C−*H*)
PMe_3	1525	−0.61		−13.15	415	
pyrimidine (κN)	1515	−0.65		−7.97	413	
CO (κC)	1580	0.32		−12.99	372	
isonitrile (κC)	1557	−0.22		−10.81	366	
η^2-benzene	1564	−0.13	4.14, 2.52	−12.75	314	
η^2-2,6-lutidine	1565	−0.07	4.11, 2.25	−12.07	310	16.0
η^2-ethyl acetate	1552			−6.99	308	
η^2-anisole	1568	−0.18	4.08, 2.22		312	16.8,1.8
			4.15, 2.32			bur
η^2-trifluorotoluene	1575	0.06	3.95, 2.30	−12.70	307	12.9
			3.77, 2.43	−13.80	305	bur
η^2-1,3-dimethoxybenzene	1561	−0.29	3.98, 2.22	−12.62	307	8.7
			4.27, 2.22	−11.17		bur
η^2-furan	1561	0.03	5.81, 4.26	−13.59	300	12.4, 4.2
			7.35, 2.81	−12.61	288	bur
η^2-acetaldehyde	1546	0.50	2.32	−8.10	300	
η^2-naphthalene	1570	0.16	3.85, 2.32	−12.89	297	9.3, 4.8
η^2-2,6-lutidinium	1592	0.68	4.13, 2.39	−11.25	296	19.0
η^2-cyclopentene	1541	0.35	3.04, 1.63	−10.3	288	13.5, 2.6
η^2-cyclopentanyl	1640	1.07		−2.56	287	
η^2-4-oxopropyl-4*H*-anisolium	1617	~1.4	4.23, 3.07	−6.2	281	14.0
η^2-3-methoxy-4*H*-anisolium	1600	1.26	4.04, 2.58	−7.31	279	9.0
η^3-allyl (C_5H_7)	1634			−7.57	273	
η^2-3*H*-2,5-dimethylpyrrole	1559	0.25	2.73	−13.21	266	12.2
η^2-nitrilium	1605	~1.1		−8.1	261	
η^2-3*H*-1,3,5-trimethylpyrrolium	1561	0.96	2.96	−11.71	255	9.6
phenyl fluoride	1596			9.30	212	
pyrrol-1-yl hydride	1590			3.81	128	
2,6-lutidin-4-yl hydride	1607			−3.66	109	

2;[13] 1,3-dimethoxybenzene, **3**; α,α,α-trifluorotoluene, **4**) were each prepared from TpW(NO)(PMe_3)Br, on a multigram scale (Table 1). The naphthalene complex **5** (Y = naphthalene) was also prepared on a small scale for comparison purposes.[14] While **1**, **2**, and **5** have been previously characterized, the dimethoxybenzene (**3**) and trifluorotoluene (**4**) complexes have not and deserve further comment.

The 1,3-dimethoxybenzene complex (**3**) is present in solution as a 3:1 equilibrium ratio of coordination diastereomers, with the metal bound across the C5−C6 double bond for both isomers. Just as is the case for the anisole analogue **2**, the major isomer of **3** has the methoxy group at C1 oriented toward the PMe_3 (isomer A). The trifluorotoluene analogue **4** exists as four isomers. The minor of these (5%) appears to be an aryl hydride, present as two atropisomers (Figure 1). Two signals at δ 9.32 and 9.35 with large H−P coupling (~100 Hz) reveal the two W−H species (similar signals were previously documented for the complex TpW(NO)(PMe_3)(H)(C_4H_4N)).[15] The major species (**4A** and **4B** (5:4 ratio)) are coordination diastereomers, each with the metal binding 3,4-η^2. Slight broadening of the proton NMR spectrum (300 MHz, 25 °C) suggests that a fluxional process occurs on a time scale similar to the NMR measurement. Presumably, this process is the intrafacial isomerization (i.e., "ring-walk" or "ring-whiz") previously observed for the benzene analogue.[7]

In order to test the ability of the precursor complexes to undergo clean substitution, each compound was dissolved in acetone-d_6 and the formation of TpW(NO)(PMe_3)(η^2-acetone-d_6) was monitored over time. Complexes **1**−**4** all undergo substitution at 20 °C with benzene being replaced most rapidly, followed by anisole, dimethoxybenzene, and trifluorotoluene in that order. The naphthalene complex **5**, which showed only 83% substitution after heating at 78 °C for 21 days, was ruled out as a useful synthon for other arene complexes. Using the most labile arene complex **1**, two different general methods were developed for the preparation of TpW(NO)(PMe_3)(L) complexes. In the first, benzene complex **1** (1 g) is dissolved in a *dry ether* solvent (DME or THF; 5−7 mL) along with 2−10 equiv of L.[16] After 6−12 h, hexanes is added to induce precipitation of the product. The second method involves stirring a suspension of the arene precursor in hexanes containing 10% of the entering ligand. While the substitution process is

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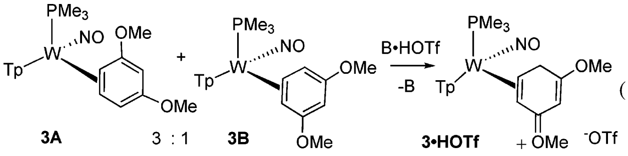
[16] The use of an ether solvent is essential, as the tungsten fragment reacts with halocarbons, alcohols, amines, esters, amides, aldehydes, and ketones.

somewhat slower (typically 1−3 days), this method often results in a cleaner product that may be directly collected on a fritted disc. Typical mass recovery ranges from 75−85% for either technique.

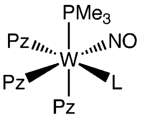
The five arene complexes were next screened for air compatibility, both as solids and in solution. Benzene complex **1** was determined to be the most susceptible to air oxidation. Complexes of trifluorotoluene (**4**), dimethoxybenzene (**3**), and anisole (**2**) have marginally improved air stability, and the naphthalene complex (**5**) was found to have the greatest air stability (see Table 1) both as a solid and in solution.

Dihapto-coordinated arene complexes have been shown previously to undergo carbon protonation with strong acids.[13] Particularly significant is the dimethoxybenzene complex **3**, which reacts with acids as weak as anilinium triflate to give the 4H-anisolium salt **3·HOTf** (eq 1), as a single isomer. ^{1}H and ^{13}C NMR data (*vide infra*) indicate that the C1 methoxy group is oriented away from the PMe$_3$, as is the case for the protonated anisole derivative.[13] This triflate salt can be recovered in high yield and is stable indefinitely as a solid. Significantly, complex **3·HOTf** is resistant to air. After 7.7 h under constant exposure to air an acetone solution of **3·HOTf** undergoes only 50% decomposition, and as a solid stored in dry air **3·HOTf** has a half-life of 41 days. Deprotonation of this complex cleanly regenerates the 3:1 mixture of **3A** and **3B**, which can cleanly deliver the {TpW(NO)(PMe$_3$)} fragment to other arenes (e.g., the preparation of anisole complex **2** or benzene complex **1** from **3·HOTf** has been carried out in quantitative yield).

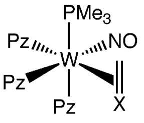


(1)

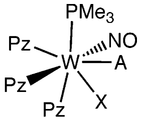
Characterization. Complexes of the form TpW(NO)(PMe$_3$)(L) are conveniently characterized by ^{1}H, ^{13}C, and ^{31}P NMR, by IR (ν_{NO}), and by cyclic voltammetry (W(I/0)). In order to identify trends that simplify their characterization, relevant data for 25 compounds have been collected in Table 2. These compounds fall into three categories: class I in which L is bound through a lone pair such as with an amine, phosphine, or isonitrile, class II, where L (C=X) coordinates through a π-bond (e.g., arene, alkene, ketone), and class III (where L = A−X), the seven-coordinate products of oxidative addition to the {TpW(NO)(PMe$_3$)} fragment (e.g., aryl hydride, aryl fluoride).



Class I



Class II



Class III

As a general guideline, class I complexes have lower NO stretching frequencies and lower anodic wave potentials ($E_{p,a}$) than class II or class III, but these values vary considerably, depending on how π-acidic the ligand is (the more π-acidic, the higher these two parameters will be). The narrow peak-width of the ^{31}P signal observed for these complexes relative to the range of observed chemical shifts makes this parameter particularly useful for monitoring the progress of reactions. However, for the provided series, the ^{31}P chemical shift does not strongly correlate with ν_{NO}, $E_{p,a}$, or the class of complex. However, we find that a significant correlation exists between the ^{183}W−^{31}P coupling constant and the class of complex. For the compounds tested, class I falls in the range 366 to 415 Hz, class II, between 255 and 314 Hz, and class III between 100 and 212 Hz. As the coordination number increases, the metal s-character in the M−P bond decreases, weakening the W−P coupling.[17] In addition, increasing the oxidation state or bond length is also known to decrease the metal−phosphine coupling.[18] In Table 2, class III complexes, which are formally W(II), have the lowest coupling constants. A plot of coupling constants versus W−P bond length for five cases where these data are available is shown in Figure 2. In related work, Cotton and Mott identified an inverse relationship between W−P bond lengths and coupling.[19]

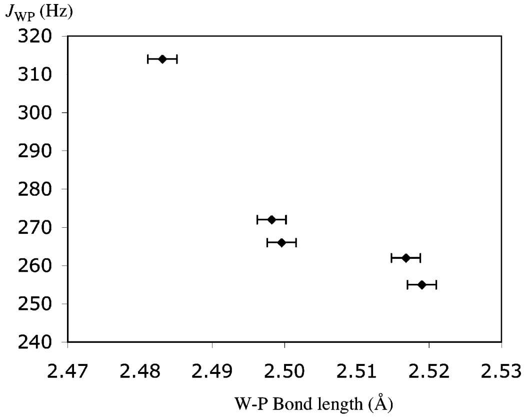


Figure 2. Plot of W−P bond distance vs $J_{P,W}$ coupling constants.[7−9,15]

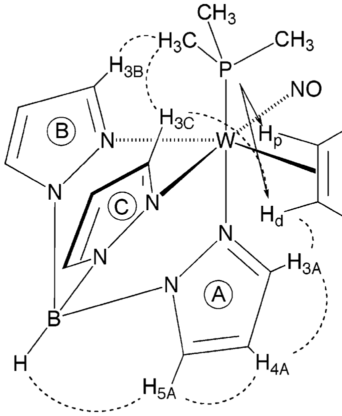


Figure 3. NOE and coupling relationships for TpW(NO)(PMe$_3$)(η^2-arene) complexes.

Determining Stereochemistry. In the majority of cases, an aromatic molecule displays planar chirality upon η^2-coordination, and two diastereomers are formed with similar spectroscopic features. The following discussion is based on crystal structures (where available) and spectroscopic data for the aromatic complexes described in Table 2. In every case observed, the aromatic is rigidly held in place by the metal with the C−C bond oriented parallel to the W−P bond. In this geometry the aromatic π^*-system can form a back-bonding interaction with the d$_\pi$-orbital that is orthogonal to the NO π^*-orbitals (see Figure 3). The resulting barrier to rotation and those associated with inter- and intrafacial isomerization result in well-resolved coordination diastereomers. The ratio of these diastereomers is governed by interactions of the aromatic ring and its

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substituents with the steric and electronic properties of the {TpW(NO)(PMe$_3$)} fragment. In particular, the interaction of the pyrazole ring trans to the nitrosyl (C in Figure 3) and the η^2-bound aromatic ring creates a steric strain that destabilizes the isomers that do not have the ring projecting over the nitrosyl group. Further, an apparent dipole moment in the {TpW(NO)(PMe$_3$)} fragment orients the negatively charged C1 methoxy of anisole or DMB toward the PMe$_3$ in complex **2** or **3**. In contrast, the cationic oxonium group of the complex **3·HOTf** is aligned *away* from the phosphine in the dominant isomer (see eq 1). ^{1}H NMR data can be used to easily differentiate these coordination diastereomers. Coupling constants between the phosphorus and the two protons attached to the bound carbons are provided in Table 2. In each case, the proton proximate to PMe$_3$ (H$_p$) has a H−C−W−P dihedral angle ranging from 57° to 73° and has a $^3J_{PH}$ in the range 8−19 Hz. In contrast, the distal proton (H$_d$) is related to the phosphorus through a dihedral angle of 94−108° and shows a much smaller $^3J_{PH}$ of 0−5 Hz. In addition, H$_d$ is nested between two pyrazole rings and experiences shielding, resulting in a ~1.5 ppm upfield shift (cf. H$_p$*)*. While the proximity of H$_d$ and H$_p$ to electronegative atoms can complicate their assignments, we have found that the *sum of their chemical shifts* is virtually identical for the two isomers. This observation, which greatly aids in the assignment of minor isomers, arises from the situation that the organic *ligands* for the two coordination diastereomers are enantiomerically related, and in the absence of the anisotropic effects of the complex they would have identical chemical shifts. The shielding effect experienced by H$_d$ in one isomer will be experienced by H$_p$ in the other isomer. Additional information regarding the stereochemistry of organic ligands formed from their aromatic precursors is gained from NOE interactions of the H3 protons of pyrazole rings A and C (Figure 3), where the latter is identified by its NOE interaction with the PMe$_3$. The pyrazole protons are readily assigned by NOE of the H5's with B−H and with COSY correlations, as shown in Figure 3.

Concluding Remarks. Complexes of the form TpW(NO)PMe$_3$(η^2-aromatic) may be prepared in multigram quantities, either from reduction of a W(I) precursor or from arene substitution. In particular, the complex [TpW(NO)PMe$_3$(η^2-DMBH)]OTf (**3·HOTf**) was found to be a suitable precursor that could be stored in the form of its conjugate acid, rendering it air-stable. Guidelines for determining coordination mode and stereochemistry for complexes of the form TpW(NO)PMe$_3$(L) have also been summarized, and among these, ^{31}P NMR spectroscopy is found to be a particularly efficient tool.

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Supporting Information Available: Synthetic details and characterization for compounds **1**−**5** and large-scale (100−250 g) syntheses of TpW(NO)(PMe$_3$)Br, TpW(NO)Br$_2$, and TpW(NO)(CO)$_2$ starting from W(CO)$_6$. This material is available free of charge via the Internet at http://pubs.acs.org.

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