and H_2O can be ruled out as we do not observe the formation of IrD. In contrast, a deuteride complex, namely, $[(triphos)IrD(O_2CCD_3)]^+$, forms together with HDO when **1** is reacted with C_2D_5OH. (ii) This reaction occurs also in CH_2Cl_2 with an equimolecular amount of ethanol. (iii) Acetaldehyde does not react with **1** in CH_2Cl_2 unless 1 equiv of a protic acid such as triflic acid is added. Then a fast reaction occurs and the *cis*-chloride–η^2-acetate derivative $[(triphos)IrCl(O_2CMe)]BPh_4$ (**8**) forms together with H_2O. (iv) When **1** (0.5 mmol) is reacted with a stoichiometric amount of C_2H_5OD and a 10-fold excess of R'CHO (R' = Pr, Bu, Ph), the formed η^2-carboxylate hydride contains the aldehyde R' group and both acetaldehyde and HDO are the coproducts. (v) In the temperature range of −60 to 20 °C, $^{31}P\{^1H\}$ NMR spectroscopy shows that the formation of **4** from C_2H_5OD is preceded by the appearance of an intermediate species. Complex **4** begins to form at −20 °C, and its concentration in solution increases as the temperature increases. Simultaneously, the concentration of the intermediate decreases until, at 0 °C, only **4** is present. The intermediate species exhibits an AMQ splitting pattern with $\delta_A = -27.38$, $\delta_M = -34.50$, and $\delta_Q = -35.48$ [$J(AM) = J(AQ) = 19.50$ Hz, $J(MQ) = 26.60$ Hz], which is typical for octahedral Ir(III) complexes containing three different ligands trans to triphos. A suitable intermediate could well be the hydroperoxo aldehyde complex A (Scheme I).

Registry No. 1, 128549-58-6; **2**, 128549-59-7; **3**, 128549-61-1; **4**, 128549-63-3; **5**, 128549-65-5; **6**, 128549-67-7; **7**, 128549-69-9; **8**, 128549-71-3; $[Ir_2Cl_2(C_8H_{14})_4]$, 12246-51-4.

Supplementary Material Available: Analytical data for the new complexes and detailed preparation and characterization of $[(triphos)IrCl(C_2H_4)]$ (1 page). Ordering information is given on any current masthead page.

Synthesis and Reactions of Tungsten(IV) Bis(imido) Complexes: Relatives of Bent Metallocenes

Darryl S. Williams, Mark H. Schofield, Jens T. Anhaus, and Richard R. Schrock*

Department of Chemistry 6-331
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received May 7, 1990

Four-coordinate tungsten(IV) or molybdenum(IV) complexes are relatively rare.[1] The core geometry of such species may be either a paramagnetic tetrahedron (e.g., $Mo(O\text{-}t\text{-}Bu)_4$[1a]), diamagnetic square plane (e.g., $W(O\text{-}2,6\text{-}C_6H_3Me_2)_4$[1b]), or a diamagnetic flattened tetrahedron (e.g., $W(S\text{-}t\text{-}Bu)_4$,[1c] $Mo(S\text{-}2,4,6\text{-}C_6H_2Me_3)_4$,[1d] or $Mo(S\text{-}t\text{-}Bu)_4$[1e]). The recent synthesis of square-planar d^4 $Os(NAr)_2(PMe_2Ph)_2$ (Ar = $2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2$)[2] raised the question as to whether analogous d^2 tungsten(IV) complexes could be prepared, and whether they would be planar or tetrahedral. We have now synthesized complexes of the type $W(NAr)_2L_2$ (L = a phosphine). They are diamagnetic, are believed to be tetrahedral species, and in contrast to $Os(NAr)_2(PMe_2Ph)_2$, react readily with π bonding ligands via five-coordinate intermediates.

$W(NAr)_2Cl_2(dme)$[3] can be reduced readily with sodium amalgam in the presence of dimethylphenylphosphine in diethyl ether to give burgundy-colored, air-sensitive $W(NAr)_2(PMe_2Ph)_2$ (**1**) in 50–60% yield.[4] ^{31}P NMR data indicate that the phosphines are not lost readily from the metal on the NMR time scale in solution ($J_{PW} = 465$ Hz). So far, complexes analogous to **1** containing PPh_3, PMe_3, or $P(OPh)_3$ instead of PMe_2Ph have not been isolated, and no crystals of **1** have been obtained yet that are suitable for X-ray studies.

$W(NAr)_2(PMe_2Ph)_2$ reacts within 1–2 min with acetone in pentane to give orange-yellow $W(NAr)_2(PMe_2Ph)(\eta^2\text{-}OCMe_2)$ (**2a**) quantitatively. An X-ray study[5] shows **2a** to be pseudotetrahedral, with W, P, O, and C lying in the pseudoplane that bisects the N–W–N angle (mean deviation of 0.034 Å; Figure 1). One imido ligand is close to linear (W–N–C = 168.8 (6)°) while the other is more bent (155.8 (5)°). Proton and carbon NMR spectra show the two imido ligands to be equivalent on the NMR time scale at 25 °C. One can rationalize the orientation of the imido groups' phenyl rings relative to each other and relative to the phosphine and acetone ligands on the basis of simple steric arguments. The C–O distance of 1.39 (1) Å suggests that **2a** is best described as an oxametallacyclopropane complex of W(VI); no ν_{CO} stretch could be observed above 1400 cm^{-1}. There are now many examples of complexes that contain a π-bound ketone or aldehyde.[6]

$W(NAr)_2(PMe_2Ph)_2$ reacts with propionaldehyde to give $W(NAr)_2(PMe_2Ph)(\eta\text{-}OCHEt)$ (**2b**), in which the two imido ligands are inequivalent and the methylene protons in propionaldehyde are diastereotopic, consistent with **2b** being analogous to **2a**. Two isomers are observed; we propose one has a structure strictly analogous to that of **2a**, and the other a structure in which the carbon atom is in the position next to phosphorus.

The result of reactions of $W(NAr)_2(PMe_2Ph)_2$ with acetylenes or olefins appears to depend largely on the size of the added ligand. $W(NAr)_2(PMe_2Ph)_2$ reacts with (trimethylsilyl)acetylene and norbornene to give $W(NAr)_2(PMe_2Ph)(HC{\equiv}CSiMe_3)$ (**2c**) and $W(NAr)_2(PMe_2Ph)(norbornene)$ (**2d**), respectively. NMR spectra are consistent with a relatively rigid core geometry analogous to that found in **2a** in which neither (trimethylsilyl)acetylene nor norbornene rotates about the ligand(centroid)–metal axis. However, $W(NAr)_2(PMe_2Ph)_2$ reacts with acetylene and ethylene to form $W(NAr)_2(PMe_2Ph)_2(C_2H_2)$ (**2e**) and $W(NAr)_2(PMe_2Ph)_2(C_2H_4)$ (**2f**), respectively. The two ends of the acetylene and ethylene ligands are equivalent in each complex by NMR down to −80 °C, as are the two phosphine ligands. All data are consistent with their being distorted trigonal bipyramids containing axial phosphine ligands and imido ligands whose phenyl rings lie in the equatorial plane. NMR data alone cannot distinguish whether acetylene and ethylene lie in the WN_2 plane or are oriented perpendicular to it. We presume that five-coordinate intermediates are formed also in the reactions that give **2c** and **2d**.

We propose that all four-coordinate d^2 complexes reported here are pseudotetrahedral, since in a tetrahedron two imido ligands (each a 2π, 1σ donor) can form the maximum number of met-

---

(1) (a) Cayton, R. H.; Chisholm, M. H.; Clark, D. L.; Hammond, C. E. *J. Am. Chem. Soc.* **1989**, *111*, 2751 and references therein. (b) Listemann, M. L.; Schrock, R. R.; Dewan, J. C.; Kolodziej, R. M. *Inorg. Chem.* **1988**, *27*, 264. (c) Listemann, M. L.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1985**, *107*, 7207. (d) Roland, E.; Walborsky, E. C.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1985**, *107*, 5795. (e) Otsuka, S.; Kamata, M.; Hirotsu, K.; Higuchi, T. *J. Am. Chem. Soc.* **1981**, *103*, 3011. (f) Chisholm, M. H.; Cotton, F. A.; Extine, M. W. *Inorg. Chem.* **1978**, *17*, 1329.

(2) Anhaus, J. T.; Kee, T. P.; Schofield, M. H., Schrock, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 1642.

(3) Schrock, R. R.; DePue, R. T.; Feldman, J.; Yap, K. B.; Yang, D. C.; Davis, W. M.; Park, L.; DiMare, M.; Schofield, M.; Anhaus, J.; Walborsky, E.; Evitt, E.; Krüger, C.; Betz, P. *Organometallics* **1990**, *9*, 2262–2275.

(4) See supplementary material for experimental details and analytical and NMR data.

(5) Crystals were mounted on glass fibers in air and coated in epoxy. Data were collected on an Enraf-Nonius CAD-4 diffractometer at room temperature using Mo Kα radiation (space group $P2_1/a$ with $a = 16.714$ (2) Å, $b = 12.343$ (1) Å, $c = 16.966$ (1) Å, $\beta = 91.909$ (7)°, $Z = 4$, FW = 730.62, and $\rho = 1.387$ g/cm^3). A total of 5011 reflections ($+h,+k,\pm l$) were collected in the range $3° < 2\theta < 55°$ with 3319 having $I > 3.00\sigma(I)$ being used in the structure refinement by full-matrix least-squares techniques (362 variables) using the TEXSAN crystallographic software package from Molecular Structure Corporation; final $R_1 = 0.037$, $R_2 = 0.037$. Full details can be found in the supplementary material.

(6) (a) Bryan, J. C.; Mayer, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 2298 and references therein. (b) Garner, C. M.; Quirôs Mêndez, N.; Kowalczyk, J. J.; Fernândez, J. M.; Emerson, K.; Larsen, R. D.; Gladysz, J. A. *J. Am. Chem. Soc.* **1990**, *112*, 5146 and references therein.

0002-7863/90/1512-6728$02.50/0

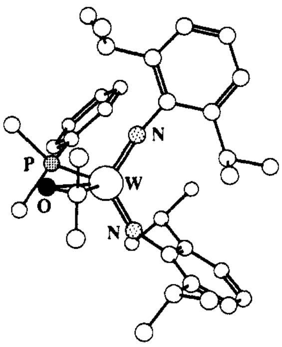


Figure 1. A view of the structure of $W(NAr)_2(PMe_2Ph)(\eta^2\text{-}OCMe_2)$: N-W-C = 108.8 (3)° and 110.8 (3)°, P-W-N = 100.6 (2)° and 106.8 (2)°, P-W-C = 113.7 (3)°, N-W-N = 116.0 (3)°, W-O = 2.025 (5) Å, W-C = 2.118 (9) Å, W-N = 1.785 (6) and 1.776 (7) Å, W-P = 2.509 (2) Å, C-O = 1.39 (1) Å.

al-nitrogen π bonds (four).[7] The $W(NAr)_2$ fragment therefore could be regarded as isolobal and isoelectronic with the $HfCp_2$ fragment, and $W(NAr)_2(PMe_2Ph)_2$ therefore is analogous to $TiCp_2(PMe_3)_2$,[8] a view that is useful in explaining the orientation of the acetone ligand in **2a** and π-bound ligands in analogous complexes. Of course an imido ligand is much more "flexible" than a Cp ligand in terms of π bonding,[9] a fact that allows $W(NAr)_2L_2L'$ complexes to form readily. Although $W(NAr)_2L_2L'$ complexes could be considered 20e species with an occupied π^* orbital, we can expect the N-W-N angle to be relatively large in order to reduce the overall W-N bond order and minimize the destabilizing effect of that configuration. This analysis is consistent with a recent crystal structure of $Os(NAr)_2I_2(PMe_2Ph)$ in which N-Os-N = 155°.[10]

On the basis of the results presented here, we can speculate that other pseudotetrahedral complexes containing the bent 14e $M(NAr)_2$ core will show certain "metallocene-like" structural preferences, but yet will react readily with donor ligands to yield five-coordinate species or substituted pseudotetrahedral bis(imido) products. Preliminary results for complexes based on the $[Re(NAr)_2]^{+}$ [11] and $[Os(NAr)_2]^{2+}$ [10] cores confirm that this is often the case. We hope to be able to explore the chemistry of a wide variety of such d^2 bis(imido) complexes, in particular chemistry that bears on the potential utility of the d^2/d^0 redox couple.

Acknowledgment. We thank the National Institutes of Health (Grant GM 31978) and the National Science Foundation (CHE 88-22508) for research support, the U.S. Department of Energy, Division of University and Industry Programs, for funds to purchase the X-ray diffractometer (Grant DE-FG05-86ER75292), Dr. W. M. Davis for collecting the data set for **2a**, and Dr. W. E. Crowe for helpful discussions. J.T.A. thanks the Deutscher Akademischer Austauschdienst for a NATO Postdoctoral Fellowship.

Supplementary Material Available: Experimental details, a description of the X-ray study, a labeled ORTEP drawing, and tables of final positional parameters and final thermal parameters for **2a** (15 pages); table of final observed and calculated structure factors for **2a** (31 pages). Ordering information is given on any current masthead page.

---

(7) If the N/W/N plane is defined to be the xz plane, then the b_1 combination of in-plane p orbitals on the two nitrogen atoms overlaps poorly with the b_1 orbital on the metal (d_{xz}) as the N-W-N angle decreases from 180°. If this interaction *is* counted as a π bond, then four are formed. Only three π bonds can form in a trans, square-planar $W(NR)_2L_2$ species.[2]

(8) Kool, L. B.; Rausch, M. D.; Alt, H. G.; Herberhold, M.; Thewalt, U.; Wolf, B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 394.

(9) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley-Interscience: New York, 1988.

(10) Kee, T. P.; Anhaus, J. T.; Schrock, R. R.; Davis, W. M.; Schofield, M. H., unpublished results.

(11) Weinstock, I. A. Ph.D. Thesis, MIT, 1990.

Tin-Directed Baeyer-Villiger and Beckmann Fragmentations

Roger P. Bakale, Mark A. Scialdone, and Carl R. Johnson*

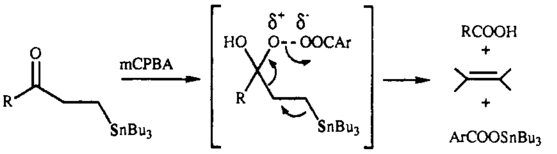
Department of Chemistry, Wayne State University
Detroit, Michigan 48202

Received May 15, 1990

The synthetic usefulness of carbon-carbon bond fragmentations of cyclic systems to give acyclic systems is limited by the degree of regiochemical control. Functionality that can exert control through transition-state stabilization is needed to achieve selectivity. We were interested in utilizing the β-effect[1] of tin[2] to direct carbon-carbon bond fragmentations that were both efficient and compatible with multiple functionalities. Since the migratory aptitudes of groups in the Baeyer-Villiger oxidations[3] and participation in Beckmann fragmentations are related to the ability of the group to stabilize a positive charge in the transition state, a tin atom β to the keto or oximino group could facilitate participation from the side where the β-stabilization could occur. The β-trimethylsilyl group has been demonstrated to exert regiochemical control in Baeyer-Villiger oxidations[4] and to favor Beckmann fragmentations over normal Beckmann rearrangements of oximes.[5,6] These directive effects of the silyl group are not completely pervasive, and in favorable cases, the "normal" products are observed.[4-6] Tin has been used to direct lead tetraacetate mediated oxidative fragmentations of β-stannyl oximes (to provide alkenes and nitrile oxides)[7] and β-stannyl carboxylic acids (to provide alkenes and carbon dioxide).[8]

The requisite β-tributylstannyl ketones were prepared by either conjugate addition of Bu_3SnM (M = Li, Cu, etc.) to α,β-unsaturated ketones[9] or alkylation of the ketone or imine enolates with ICH_2SnBu_3.[10] The β-tributylstannyl oximes were prepared by treatment of the β-tributylstannyl ketones with hydroxylamine. Both syn and anti oximes (with respect to tin) were obtained except where the ketone had α-substitution which directed the oxime formation exclusively anti.

Treatment of β-tributylstannyl ketones with 3-chloroperoxybenzoic acid (mCPBA) resulted in a tin-directed oxidative fragmentation to give carboxylic acids (eq 1). It can be seen that



(1)

the β-tributylstannyl group is the dominant group for controlling the regiochemical selectivity in these oxidations (Table I).[11] The

---

(1) The term β-effect refers to the ability of tin (and related atoms) to stabilize cationic character at a β position presumably by electron delocalization from the C-Sn σ-bond into the empty β p orbital. For a recent discussion of such effects, see: Lambert, J. B.; Wang, G.-t.; Teramura, D. H. *J. Org. Chem.* **1988**, *53*, 5422-5428.

(2) For recent reviews on organotin chemistry, see: Pereyre, M.; Quintard, J.-P.; Rahm, A. *Tin in Organic Synthesis*; Butterworths: London, 1987. Sato, T. *Synthesis* **1990**, 259-270.

(3) Hassall, C. H. *Org. React.* (*N.Y.*) **1957**, *9*, 73-106.

(4) (a) Hudrlik, P. F.; Hudrlik, A. M.; Nagendrappa, G.; Yimenu, T.; Zellers, E. T.; Chin, E. *J. Am. Chem. Soc.* **1980**, *102*, 6894. (b) See also: Asaoke, M.; Takenouchi, K.; Takei, H. *Tetrahedron Lett.* **1988**, *29*, 325.

(5) (a) Nishiyama, H.; Sakuta, K.; Osaka, N.; Itoh, K. *Tetrahedron Lett.* **1983**, *24*, 4021. (b) Nishiyama, H.; Sakuta, K.; Osaka, N.; Arai, H.; Matsumoto, M.; Itoh, K. *Tetrahedron* **1988**, *44*, 2413.

(6) Hudrlik, P. F.; Waugh, M. A.; Hudrlik, A. M. *J. Organomet. Chem.* **1984**, *271*, 69.

(7) Nishiyama, H.; Arai, H.; Ohki, T.; Iton, K. *J. Am. Chem. Soc.* **1985**, *107*, 5310.

(8) Nishiyama, H.; Matsumoto, M.; Arai, H.; Sakaguchi, H.; Itoh, K. *Tetrahedron Lett.* **1986**, *27*, 1599.

(9) Still, W. C. *J. Am. Chem. Soc.* **1977**, *99*, 4836. Piers, E.; Morton, H. E. *J. Chem. Soc., Chem. Commun.* **1978**, 1033. Lipshutz, B. H; Ellsworth, E. E.; Dimock, S. H.; Reuter, D. C. *Tetrahedron Lett.* **1989**, *30*, 2065.

(10) Seyferth, D.; Andrews, S. B. *J. Organomet. Chem.* **1971**, *30*, 151-166.

(11) New compounds were fully characterized spectroscopically and by microanalysis and/or HRMS.

0002-7863/90/1512-6729$02.50/0