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Synthesis of Stable Tungsten(VI) Imido Alkylidene Complexes: Crystal Structure of an Air-Stable Cationic Alkylidene Complex

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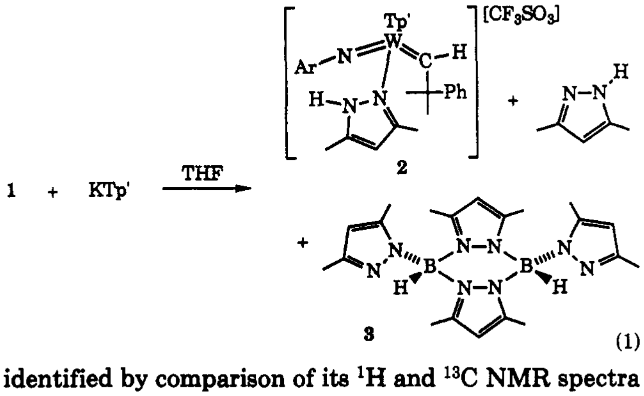
Summary: Synthesis of remarkably air-, moisture-, and heat-stable tungsten(VI) imido alkylidenes has been achieved by addition of potassium hydrotris(1-pyrazolyl)borate (KTp) or potassium hydrotris(3,5-dimethyl-1-pyrazolyl)borate (KTp′) to $W(CHC(CH_3)_2Ph)(NAr)(OTf)_2(DME)$ (1; Ar = 2,6-*i*-Pr_2-C_6H_3, OTf = SO_3CF_3, DME = $CH_3OCH_2CH_2OCH_3$). Addition of KTp′ to 1 yielded $[Tp'W(CHC(CH_3)_2Ph)(NAr)(pyrH)][OTf]$ (2; pyrH = 3,5-dimethylpyrazole), which is the first crystallographically characterized d^0 cationic alkylidene. Compound 1 reacts with KTp to give $TpW(CHC(CH_3)_2Ph)(NAr)(OTf)$ (5), which, in the presence of $AlCl_3$, catalyzes the ring-opening metathesis polymerization of cyclooctene, yielding high-molecular-weight poly(1-octenylene) (M_n = 98 900, M_w/M_n = 1.2).

We have been interested in the development of exceptionally air- and heat-stable tungsten(VI) alkylidenes for the catalysis of acyclic diene metathesis (ADMET) polymerizations.[1,2] Compounds exhibiting such stability have been shown to be efficient catalysts for the ring-opening metathesis polymerizations (ROMP) of cyclic olefins in air.[1] In a search for a synthetically facile route to cationic materials of this type with potentially greater olefin affinity, we have investigated the reaction of tris-chelating pyrazolylborate ligands with the known compound $W(CHC(CH_3)_2Ph)(NAr)(OTf)_2(DME)$[3] (1; Ar = 2,6-*i*-$Pr_2$-$C_6H_3$, Ph = C_6H_5, OTf = SO_3CF_3, DME = $CH_3OCH_2CH_2OCH_3$). We report here the synthesis of three new tungsten(VI) imido alkylidene complexes, including an unprecedented air- and heat-stable cationic alkylidene complex.

Addition of 1 equiv of the potassium salt of the tris-chelating, monoanionic ligand hydrotris(3,5-dimethyl-1-pyrazolyl)borate (KTp′)[4] to a cold, stirred THF solution of 1 gave the six-coordinate cationic tungsten(VI) imido alkylidene pyrazole Tp′ complex 2 (yield 10.8% based on 1), shown in eq 1. The pyrazabole side product 3 was identified by comparison of its ^1H and ^{13}C NMR spectra with literature spectra.[5] Proton-catalyzed decomposition of pyrazolylborates to pyrazaboles has been previously reported.[6] Presumably, the strongly electron-deficient tungsten center of 1 acts as a Lewis acid to facilitate KTp′ decomposition in this reaction.



(1)

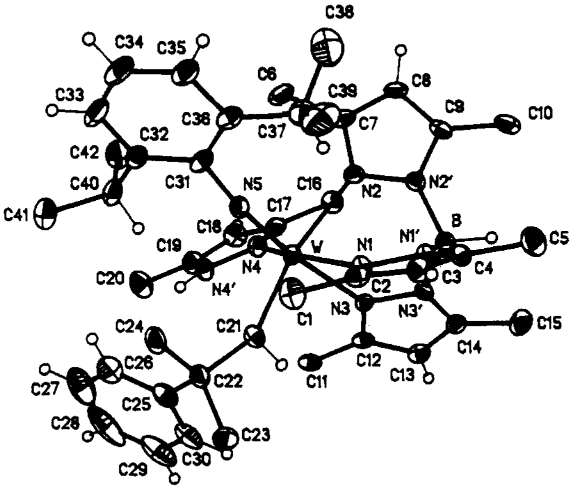


Figure 1. Molecular structure of 2, showing 50% thermal ellipsoids and the atom-labeling scheme. Selected bond distances (Å): W–C(21), 1.964 (9); W–N(5), 1.752 (6); W–N(4), 2.189 (6); W–N(1), 2.179 (6); W–N(2), 2.305 (7); W–N(3), 2.311 (6). Selected bond angles (deg): W–C(21)–C(22), 149.0 (6); W–N(5)–C(31), 173.5 (7); N(5)–W–C(21), 100.2 (3); N(5)–W–N(4), 99.1 (3); C(21)–W–N(4), 95.1 (3).

Eight high-oxidation-state, cationic tungsten alkylidenes have previously been reported.[7] These five-coordinate complexes were characterized as extremely sensitive to Lewis base solvents, such as Et_2O and THF. The cationic imido neopentylidenes[7b] were more thermally stable (60 °C in $CDCl_3$) than their oxo analogs (25 °C in $CDCl_3$). In contrast, 2 was found to be completely stable indefinitely both in the solid state and in solution in moist air. No ^1H NMR evidence of thermal decomposition was observed when 2 was heated as a solid to 180 °C in air.

The ^1H NMR spectrum[8] of 2 was consistent with the proposed structure, assuming free rotation of the neophylidene phenyl but no rotation about the C–N bond of the arylimido ligand at room temperature. The alkylidene proton resonated at 11.34 ppm ($^1J_{WH}$ = 5 Hz), and the alkylidene α-carbon resonated at 297.8 ppm in the ^{13}C NMR spectrum[8] ($^1J_{CW}$ = 155 Hz, $^1J_{CH}$ = 115 Hz). High-temperature ^1H NMR spectroscopy gave no evidence for thermally induced dissociation of the coordinated pyrazole or for rotation of the arylimido ligand at temperatures up to 160 °C. A minor rotational isomer of the neophylidene (δ 11.58; $^1J_{WH}$ = 12 Hz) of 2 was observed to grow into the spectrum,[8] beginning at 60 °C. At 90 °C, an equilibrium ratio of 1.9:1 was rapidly established. Coalescence of the

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[1] Blosch, L. L.; Abboud, K.; Boncella, J. M. *J. Am. Chem. Soc.* **1991**, *113*, 7066.

[2] Blosch, L. L.; Gamble, A. S.; Boncella, J. M. *J. Mol. Catal.*, in press.

[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.

[4] Trofimenko, S. *Acc. Chem. Res.* **1971**, *4*, 17.

[5] Niedenzu, K.; Niedenzu, P. M. *Inorg. Chem.* **1984**, *23*, 3713.

[6] (a) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 4948. (b) Trofimenko, S. *J. Am. Chem. Soc.* 1967, 89, 3170.

[7] (a) Wengrovius, J. H.; Schrock, R. R. *Organometallics* **1982**, *1*, 148. (b) Pederson, S. F.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 7483.

[8] Complete NMR spectra are contained in the supplementary material.

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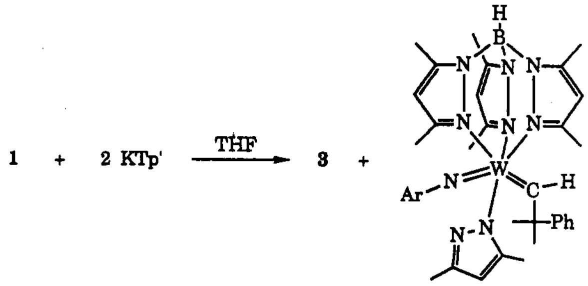
alkylidene rotamer signals was not achieved prior to decomposition, but a rotational barrier of greater than 19 kcal/mol[9] was calculated. At 160 °C, decomposition of both rotamers of 2 ensued. Compound 2 was further characterized by infrared spectroscopy (ν_{NH} = 3348 cm^{-1}) as well as by a single-crystal X-ray diffraction study.[10]

The structure of 2 consisted of well-separated molecules with pseudooctahedral coordination geometry at tungsten, as shown in the ORTEP drawing in Figure 1. Geometric constraints of the Tp′ ligand require that the imido, alkylidene, and pyrazole ligands be mutually cis.[11] No other cationic tungsten(VI) alkylidene has been previously crystallographically characterized. The W=N and W=C bond distances of 1.752 (6) and 1.964 (9) Å, respectively, are well within the normal range for six-coordinate imido alkylidenes.[12] The W–N distances for the Tp′ ligand vary from 2.179 (6) to 2.311 (6) Å and are consistent with a decreasing trans influence of the ligands imido ≥ alkylidene > pyrazole.[13] Although the W–C(21)–C(22) angle of 149.0 (6)° is somewhat large and might imply an agostic interaction between the metal center and the alkylidene α-H,[14] the ^{1}H–^{13}C coupling constant of 115 Hz is normal[14,15] for this W–C–C angle and gives no evidence for interaction between the tungsten center and the alkylidene α-H. Since the formal electron count at tungsten is 18 electrons, an α-agostic interaction is not expected. Steric interactions of the arylimido isopropyl groups, Tp′ 3-methyl groups, and the neophyl group may account for the large W–C(21)–C(22) angle.

Attempts to increase the yield of 2 by adding a second equivalent of KTp′ resulted in formation of 4, Tp′W(CHC(CH$_3$)$_2$Ph)(NAr)(pyr) (pyr = 3,5-dimethylpyrazolide), the neutral analog of 2 (yield 65.5% based on 1), as shown in eq 2. Compound 4 was distinguished by the conspicuous absences of a pyrazole proton resonance in the ^{1}H NMR spectrum and an N–H stretch in the infrared spectrum, as compared to the spectra of 2. The alkylidene resonance was shifted to 10.79 ppm in the ^{1}H NMR spectrum[8] and to 292.1 ppm ($^1J_{CW}$ = 166.9 Hz, $^1J_{CH}$ = 118.2 Hz) in the ^{13}C NMR spectrum.[8] Like 2, 4 exhibited remarkable air, moisture, and heat stability.[16] The interconversion of 2 and 4 was readily achieved by addition of *n*-BuLi to 2 and protonation of 4 with triflic acid.



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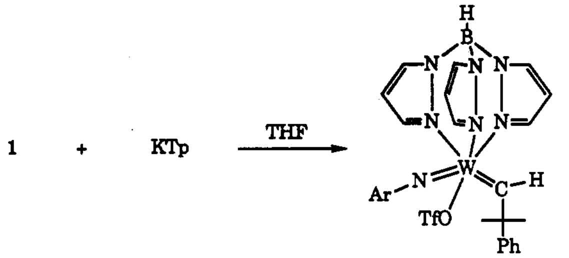
(2)

In contrast to the reactivity observed for addition of KTp′ to 1, the reaction of equimolar amounts of potassium hydrotris(1-pyrazolyl)borate (KTp)[4] and 1 in THF solution at ambient temperature resulted in rapid formation of TpW(CHC(CH$_3$)$_2$Ph)(NAr)(OTf) (5; eq 3) (yield 90.1% based on 1). No evidence of decomposition of Tp was detected in the crude product. Perhaps the reduced steric demands of Tp vs those of Tp′ facilitates rapid coordination, to the exclusion of competing decomposition processes.[17]



5

(3)

As with 2 and 4, compound 5 exhibited remarkable air and heat stability.[18] The complex is stable in the air as a solid indefinitely and can be recrystallized in the air by slow evaporation of Et$_2$O. The complex showed no evidence of decomposition by ^{1}H NMR spectroscopy up to 160 °C in C$_6$D$_5$Br. The ability of Tp and Tp′ to impose octahedral geometry[19] as well as the increased steric bulk and the formal 18-electron count at tungsten likely contribute to the robust nature of these compounds in comparison to other tungsten(VI) imido alkylidene compounds.[3,7b,20]

The ^{1}H NMR spectrum[8] of 5 at 25 °C indicates two isomers (5:1) due to rotation about the W=C bond. The neophylidene proton signals for the major and minor isomers resonate at 11.38 ppm ($^2J_{WH}$ = 4 Hz) and 11.45 ppm ($^2J_{WH}$ = 10 Hz), respectively (^{13}C NMR: major isomer, δ 300.5 ($^1J_{CW}$ = 152 Hz, $^1J_{CH}$ = 118 Hz); minor isomer, δ 292.8). The signal for the minor rotamer disappears upon warming above 100 °C, commensurate with a barrier to rotation of greater than 19 kcal/mol.[9] The proton signals of the 2,6-*i*-Pr$_2$-C$_6$H$_3$ group of the major isomer are broadened, suggesting hindered rotation about the nitrogen–carbon bond of the imido ligand. Coalescence measurements revealed a barrier to rotation of 15 kcal/mol. The fact that facile rotation is observed for 5 and not for 2 or 4 is indicative of the reduced steric congestion of Tp relative to that of Tp′.

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(9) Several recent studies have appeared in which the barriers to rotational isomerism of group 6 alkylidenes have been experimentally determined. These studies involve four- and five-coordinate, electronically unsaturated alkylidene complexes but not six-coordinate, 18-electron complexes: (a) Schrock, R. R.; Crowe, W. E.; Bazan, G. C.; DiMare, M.; O'Regan, M. B.; Schofield, M. H. *Organometallics* **1991**, *10*, 1832. (b) Schrock, R. R.; Murdzek, J. S.; Bazan, G.; Robbins, J.; DiMare, M.; O'Regan, M. B. *J. Am. Chem. Soc.* **1990**, *112*, 3875. (c) Schrock, R. R.; DuPue, R. T.; Feldman, J.; Yap, K. B.; Yang, D. C.; Davis, W. M.; Park, L. Y.; DiMare, M.; Schofield, M.; Anhaus, J.; Walborsky, E.; Evitt, E.; Krüger, C.; Betz, P. *Organometallics* **1990**, *9*, 2262. (d) Kress, J.; Osborn, J. *J. Am. Chem. Soc.* **1987**, *109*, 3953.

(10) Crystal data for C$_{43}$H$_{59}$BF$_3$N$_9$O$_3$SW: monoclinic, $P2_1/c$, a = 9.739 (4) Å, b = 18.799 (3) Å, c = 25.379 (8) Å, β = 97.33 (3)°, V = 4608 (2) Å^3, Z = 4, D_{calcd} = 1.49 g/cm^3, Mo Kα (λ = 0.71069 Å), T = 298 K. The structure was solved by the heavy-atom method in SHELXTL PLUS, from which the location of the W atom was obtained. The rest of the nonhydrogen atoms were obtained from a subsequent difference Fourier map. The structure was refined in SHELXTL PLUS using full-matrix least squares, yielding values for R and R_w of 3.53 and 3.89, respectively, from 3963 reflections with $I > 3\sigma(I)$. Sheldrick, G. M. SHELXTL PLUS; Nicolet XRD Corp., Madison, WI, 1990.

(11) Brower, D. C.; Templeton, J. L.; Mingos, D. M. P. *J. Am. Chem. Soc.* **1987**, *109*, 5203.

(12) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley-Interscience: New York, 1988; pp 182–184.

(13) See ref 12, pp 156–157.

(14) (a) Edwards, D. S.; Biondi, L. V.; Ziller, J. W.; Churchill, M. R.; Schrock, R. R. *Organometallics* **1983**, *2*, 1505. (b) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98. (c) See also ref 12, p 155.

(15) See ref 12, p 134.

(16) Compound 4 was stable to air and moisture, both in the solid phase and in solution, for an indefinite period. As a solid, 4 is stable to 210 °C in air.

(17) Frauendorfer, E.; Brunner, H. *J. Organomet. Chem.* **1982**, *240*, 371.

(18) Compound 5 has a melting point of 205–210 °C dec in the air and has been stored in the air for 3 months with no evidence of decomposition by ^{1}H NMR spectroscopy.

(19) Curtis, M. D.; Shiu, K.-B. *Inorg. Chem.* **1985**, *24*, 1213.

(20) Johnson, L. K.; Virgil, S. C.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 5384.

Compounds 2, 4, and 5 were found to be inert toward the metathesis of cyclooctene or 1,9-decadiene, even in refluxing monomer. However, a mixture of 5 and $AlCl_3$ rapidly catalyzes ring-opening metathesis polymerization of cyclooctene at 25 °C either under N_2 or in the air, forming high-molecular-weight poly(1-octenylene) within minutes.[21] The activity of this system is akin to that of $Tp'W(CHC(CH_3)_3)(O)Cl/AlCl_3$, which we have previously reported.[1] A mixture of 5 and $AlCl_3$ showed limited activity for the acyclic diene metathesis polymerization of 1,9-decadiene over a 12-h period at 90 °C.[22]

Acknowledgment is made to the National Science Foundation (Grant No. DMR-8912026) and to Shell Development Corp. for support of this research.

Supplementary Material Available: Text giving synthetic details for the preparation of 2, 4, and 5 and complete ^1H NMR and ^{13}C NMR data for 2, 4, and 5 and tables of thermal parameters, positional parameters, and bond lengths and angles as well as details of the X-ray crystal structure determination of 2 (20 pages). Ordering information is given on any current masthead page.

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[21] Polymer prepared under an N_2 atmosphere: $M_n = 98900$, $M_w/M_n = 1.2$. Polymer prepared in air: $M_n = 90000$, $M_w/M_n = 1.2$.

[22] Approximately 5% internal olefin was formed, as indicated by ^1H NMR spectroscopy of the reaction mixture.

Synthesis of Osmium *meso*-Tetra-*p*-tolylporphyrin Carbene Complexes (TTP)Os=CRR′ (R, R′ = *p*-Tolyl; R = H, R′ = $SiMe_3$, CO_2Et): Stereoselective, Catalytic Production of Olefins from Substituted Diazomethanes

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Summary: A series of osmium *meso*-tetra-*p*-tolylporphyrin carbene complexes, (TTP)Os═CRR′ [R, R′ = *p*-tolyl (1); R = H, R′ = $SiMe_3$ (2), CO_2Et (3)], have been prepared by treating $[Os(TTP)]_2$ with the appropriate diazoalkane (N_2CRR'). The carbene complexes, 1–3, and the osmium complexes $[Os(TTP)]_2$, Os(TTP)(CO)(py), and $Os(TTP)(py)_2$ catalytically convert ethyl diazoacetate to diethyl maleate and diethyl fumarate in high yields and high stereoselectivity. The *Z*/*E* ratios range from 18:1 to 26:1. Olefin also can be produced from $N_2C(p\text{-}C_6H_4\text{-}CH_3)_2$ but not from $N_2CHSiMe_3$.

Although the organometallic chemistry of metalloporphyrins has developed rapidly over the past few years,[2] work in this area involving osmium porphyrin complexes has received less attention. Moreover, while various metalloporphyrins catalyze the production of olefins,[3] cyclopropanes,[4] and the oxidative carbonylation of amines,[5] use of osmium porphyrins for catalytic reactions has been limited thus far to oxidations of alkenes.[6] We have recently begun studies on organometallic osmium porphyrin compounds. Subsequent to our preparation of the first osmium porphyrin silylene complexes,[7] we turned our attention to the reaction of these complexes with diazo reagents. We report herein the synthesis of a series of new osmium porphyrin carbene complexes and the highly stereoselective, catalytic formation of olefins from diazo compounds.

As a potential new route for the formation of coordinated silene ligands ($\eta^2\text{-}R_2Si{=}CR_2$), the porphyrin silylene complex $(TTP)Os{=}SiEt_2{\cdot}THF$[8] was treated with di-*p*-tolyldiazomethane. However, the reaction resulted in displacement of the silylene ligand and formation of the carbene complex $(TTP)Os{=}C(p\text{-}C_6H_4\text{-}CH_3)_2$. A more direct method for preparing these compounds involves treating $[Os(TTP)]_2$[9] with the appropriate diazoalkane, as shown in eq 1. In a typical reaction, $(TTP)Os{=}C(p\text{-}C_6H_4\text{-}CH_3)_2$ (1) was prepared under N_2 by adding a benzene solution (3 mL) of di-*p*-tolyldiazomethane (8.3 mg, 37.4 μmol) to a stirred solution of $[Os(TTP)]_2$ (32.0 mg, 18.6 μmol) in benzene (6 mL). After 1 h, the solution was passed through a neutral alumina column and impurities were eluted with benzene. The carbene complex was washed from the column with benzene/THF (20:1 v/v). Removal of the solvent under reduced pressure yielded 37.6

$$\tfrac{1}{2}[Os(TTP)]_2 + N_2CRR' \longrightarrow (TTP)Os{=}CRR' + N_2 \qquad (1)$$

1, R = R′ = $p\text{-}C_6H_4\text{-}CH_3$
2, R = H, R′ = $SiMe_3$
3, R = H, R′ = CO_2Et

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[1] 1990–1995 Presidential Young Investigator.

[2] (a) For lead references, see: Collman, J. P.; Brothers, P. J. *Acc. Chem. Res.* **1986**, *19*, 209. (b) Wayland, B. B. *Polyhedron* **1988**, *7*, 1545. (c) Woo, L. K.; Hays, J. A.; Jacobson, R. A.; Day, C. L. *Organometallics* **1991**, *10*, 2102. (d) Arnold, J.; Hoffman, C. G. *J. Am. Chem. Soc.* **1990**, *112*, 8620. (e) Collman, J. P.; Brothers, P. J.; McElwee-White, L.; Rose, E.; Wright, L. J. *J. Am. Chem. Soc.* **1985**, *107*, 4570. (f) Collman, J. P.; Brothers, P. J.; McElwee-White, L.; Rose, E. *J. Am. Chem. Soc.* **1985**, *107*, 6110.

[3] Venberg, G. D. Ph.D. Dissertation, Stanford University, 1990.

[4] (a) Maxwell, J. L.; O'Malley, S.; Brown, K. C.; Kodadek, T. *Organometallics* **1992**, *11*, 645. (b) Callot, H. J.; Piechocki, C. *Tetrahedron Lett.* **1980**, 3489. (c) Callot, H. J.; Metz, F.; Piechocki, C. *Tetrahedron* **1982**, 2365. (d) Callot, H. J.; Schaeffer, E. *Nouv. J. Chim.* **1980**, *4*, 311. (e) Doyle, M. P. *Chem. Rev.* **1986**, *86*, 919. (f) Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411. (g) O'Malley, S.; Kodadek, T. *Tetrahedron Lett.* **1991**, *32*, 2445. (h) Maxwell, J.; Kodadek, T. *Organometallics* **1991**, *10*, 4.

[5] Leung, T. W.; Dombek, B. D. *J. Chem. Soc., Chem. Commun.* **1992**, 205.

[6] Che, C.-M.; Chung, W.-C. *J. Chem. Soc., Chem. Commun.* **1986**, 386.

[7] Woo, L. K.; Smith, D. A.; Young, V. G. *Organometallics* **1991**, *10*, 3977.

[8] Abbreviations: TTP is *meso*-tetra-*p*-tolylporphyrinato, THF is tetrahydrofuran, and py is pyridine.

[9] Collman, J. P.; Barnes, C. E.; Woo, L. K. *Proc. Natl. Acad. Sci. U.S.A.* **1983**, *80*, 7684.