Technetium-Carbon Multiple Bonds: Synthesis and Structure of Tc(=C=CHPh)Cl(dppe)$_2$ and [Tc(≡C—CH$_2$-*t*-Bu)Cl(dppe)$_2$]$^+$

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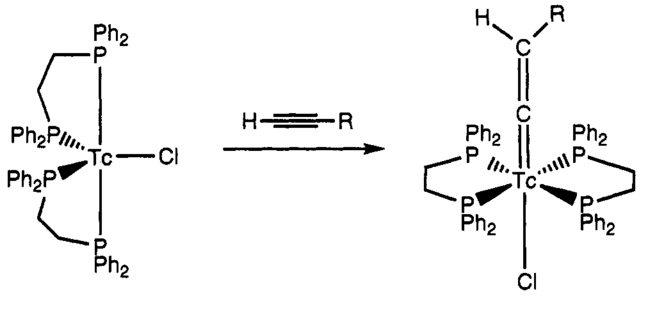
Summary: The 16-electron complex TcCl(dppe)$_2$ reacts with terminal alkynes to form neutral vinylidene complexes of the type Tc(=C=CHR)Cl(dppe)$_2$ (R = Ph, Me, t-Bu). Treatment of these vinylidene complexes with acid (HBF$_4$ for R = Ph, HNMe$_3$BPh$_4$ for R = t-Bu) yields the respective terminal carbyne complexes Tc(≡CCH$_2$R)-Cl(dppe)$_2^+$ (R = Ph, t-Bu). These vinylidene and carbyne compounds represent the first examples of technetium carbenes or carbynes. X-ray structures of Tc(=C=CHPh)Cl(dppe)$_2$ and Tc(≡CCH$_2$-t-Bu)Cl(dppe)$_2^+$ were determined, and the Tc—C bond lengths obtained were 1.861(9) and 1.724(7) Å, respectively.

Transition-metal carbene[1] and carbyne[2] complexes can be prepared by a number of routes, and as a result well-characterized carbene and carbyne complexes are known for almost all of the transition metals. A notable exception to this is technetium. Until this report, no complexes containing technetium-carbon multiple bonds had been reported.[1n] Herein we report the synthesis and structures of the first vinylidene and carbyne complexes of technetium.

Recently we isolated and characterized a stable 16-electron complex of Tc(I), TcCl(dppe)$_2$ (dppe = 1,2-bis(diphenylphosphino)ethane).[3] This compound is proving to have a rich chemistry, undergoing facile reactions with a variety of small molecules. Reactions of TcCl(dppe)$_2$ with terminal alkynes proceed rapidly at room temperature. For example, the addition of a 1 equiv of phenylacetylene to a THF solution of TcCl(dppe)$_2$ results in a complete change in color of the solution, from green to orange. The orange is due to the formation of the neutral vinylidene complex Tc(=C=CHPh)Cl(dppe)$_2$.[4] The reaction of TcCl(dppe)$_2$ with terminal alkynes appears to be quite general, in that both aryl and alkyl (methyl,[5] *tert*-butyl[6]) substituted alkynes react with TcCl(dppe)$_2$ to give terminal vinylidene complexes in high yield (Scheme 1). Also, the same products are obtained if an excess of the

Scheme 1



R = Ph, Me, ^{t}Bu

[●] Abstract published in *Advance ACS Abstracts*, March 1, 1994.

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(2) Review of carbyne complexes: (a) Kim, H. P.; Angelici, R. J. *Adv. Organomet. Chem.* **1987**, *27*, 51. (b) Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schrock, R. R.; Schubert, U.; Weiss, K. *Carbyne Complexes*; VCH Publishers: Weinheim, Germany, 1988. (c) Fischer, E. O.; Schubert, U.; Fischer, H. *Pure Appl. Chem.* **1978**, *50*, 857. (d) Schrock, R. R. *Acc. Chem. Res.* **1986**, *19*, 342. (e) Schrock, R. R. *J. Organomet. Chem.* **1986**, *300*, 249. (f) Green, M. *J. Organomet. Chem.* **1986**, *300*, 93. (g) Buhro, W. E.; Chisholm, M. H. *Adv. Organomet. Chem.* **1987**, *27*, 311. (h) Chisholm, M. H.; Conroy, B. K.; Eichhorn, B. W.; Folting, K.; Hoffmann, D. M.; Huffman, J. C.; Marchant, N. S. *Polyhedron* **1987**, *6*, 783. (i) Stone, F. G. A. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 89. (j) Stone, F. G. A. *Adv. Organomet. Chem.* **1990**, *31*, 53. (k) Pombeiro, A. J. L. *J. Organomet. Chem.* **1988**, *358*, 273. (l) Pombeiro, A. J. L. *Polyhedron* **1986**, *8*, 1595. (m) Mayr, A.; Hoffmeister, H. *Adv. Organomet. Chem.* **1991**, *32*, 227-324.

(3) Burrell, A. K.; Bryan, J. C.; Kubas, G. J. *J. Am. Chem. Soc.*, in press.

(4) Tc(=C=CHPh)Cl(dppe)$_2$: Phenylacetylene (5 mg, 0.05 mmol) was added to a solution of TcCl(dppe)$_2$ (50 mg, 0.05 mmol) in THF (5 mL). The solution changed from green to orange within a few minutes. Addition of hexane precipitated the product as an orange solid (54 mg, 98%). The product can be further purified by recrystallization from THF/hexane. IR (Nujol mull, cm^{-1}): 1572, 1540 ($\nu_{C=C}$). ^{1}H NMR (C$_6$D$_5$CD$_3$, 295 K): δ 6.0-7.8 (m, C$_6$*H*$_5$, 45 H), 2.80 (m, C*H*Ph, 1 H), 2.64 (m, PC*H*$_2$, 4 H), 2.44 (m, PC*H*$_2$, 4 H). ^{13}C NMR (THF-*d*$_8$, 295 K): δ 281 (b, Tc=*C*), 138.6-120.6 (m, Ph (dppe + vinylidene)) 109.2 (s, C=*C*HPh), 30.0 (m, P*C*H$_2$). Anal. Calcd for C$_{60}$H$_{54}$ClP$_4$Tc: C, 69.8; H, 5.27. Found: C, 70.01; H, 5.42.

(5) Tc(=C=CHMe)Cl(dppe)$_2$: Propyne was bubbled through a solution of TcCl(dppe)$_2$ (50 mg, 0.05 mmol) in THF (5 mL) for 30 s, and then the flask was sealed. The solution changed from green to orange-yellow within a few minutes. Addition of hexane precipitated the product as a yellow solid (43 mg, 83%). The product can be further purified by recrystallization from THF/hexane. IR (Nujol mull, cm^{-1}): 1582 ($\nu_{C=C}$). ^{1}H NMR (C$_6$D$_5$CD$_3$, 295 K): δ 7.4-7.0 (m, C$_6$*H*$_5$, 40 H), 2.63 (m, PC*H*$_2$, 4 H), 2.60 (m, PC*H*$_2$, 4 H), 1.82 (m, C*H*, 1 H), 0.48 (d, C*H*$_3$, 3H, $^3J_{HH}$ = 7.5 Hz). Anal. Calcd for C$_{55}$H$_{52}$ClP$_4$Tc: C, 68.08; H, 5.4. Found: C, 68.37; H, 5.61.

(6) Tc(=C=CH-*t*-Bu)Cl(dppe)$_2$: 3,3-Dimethylbutyne (4 mg, 0.05 mmol) was added to a solution of TcCl(dppe)$_2$ (50 mg, 0.05 mmol) in THF (5 mL). The solution changed from green to orange-red within a few minutes. Addition of hexane precipitated the product as an orange solid (51 mg, 94%). The product can be further purified by recrystallization from THF/hexane. IR (Nujol mull, cm^{-1}): 1576 ($\nu_{C=C}$). ^{1}H NMR (C$_6$D$_5$-CD$_3$, 295 K): δ 7.5-6.9 (m, C$_6$*H*$_5$, 40 H), 3.22 (m, C*H*, 1 H), 2.71 (m, PC*H*$_2$, 4 H), 2.56 (m, PC*H*$_2$, 4 H), 0.48 (s, *t*-Bu, 9H). ^{13}C NMR (THF-*d*$_8$, 295 K): δ 223.6 (b, Tc=*C*), 140.8 (m, Ph), 138.5 (m, Ph), 129.5 (s, C=*C*H-*t*-Bu), 128.8 (m, Ph), 127.6 (m, Ph), 33.1 (s, *C*Me$_3$), 31.0 (s, C*C*H$_3$), 30.5 (m, P*C*H$_2$). Anal. Calcd for C$_{58}$H$_{58}$ClP$_4$Tc: C, 68.81; H, 5.77. Found: C, 69.00; H, 5.87.

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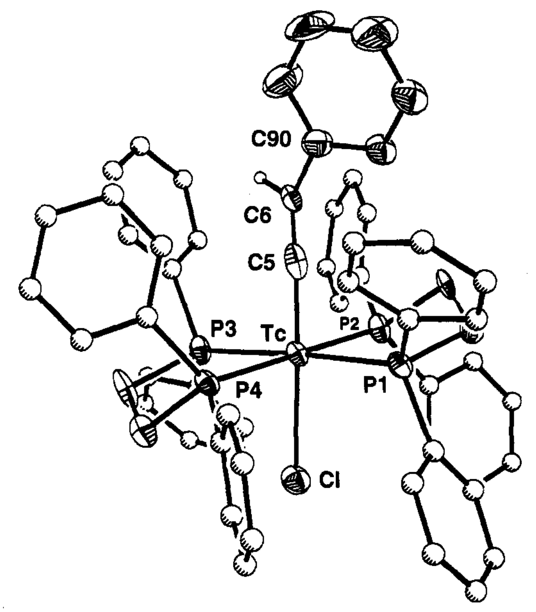


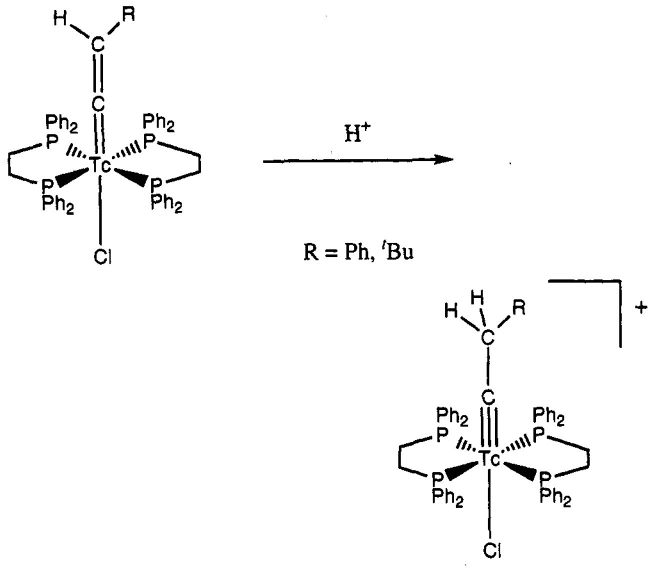
Figure 1. ORTEP representation with 50% probability ellipsoids (isotropically refined atoms are represented by shaded (carbon) or open (hydrogen) circles) of Tc(=C=CHPh)Cl(dppe)$_2$. Selected bond lengths (Å) and angles (deg) are as follows: Tc–C(5) = 1.861(9), C(5)–C(6) = 1.265(13), Tc–Cl = 2.573(3), Tc–P(1) = 2.427(3), Tc–P(2) = 2.397(2), Tc–P(3) = 2.423(3), Tc–P(4) = 2.434(2); Cl–Tc–C(5) = 177.7(3), Tc–C(5)–C(6) = 173.0(8), P(1)–Tc–C(5) = 92.4(3), P(2)–Tc–C(5) = 82.0(2), P(3)–Tc–C(5) = 90.7(2), P(4)–Tc–C(5) = 98.6(2).

alkyne is used in the reaction. No other products, such as the η^2-alkyne or hydride–acetylide complexes, could be detected.

The spectroscopic data for the new complexes are consistent with the presence of terminal vinylidene ligand. The $\nu_{C=C}$ stretch is evident in the IR spectra in the region 1540–1582 cm^{-1}. The most indicative piece of spectroscopic evidence is obtained using ^{13}C NMR spectroscopy. The α-carbon signals for Tc(=C=CHPh)Cl(dppe)$_2$ and Tc(=C=CH-*t*-Bu)Cl(dppe)$_2$ are present as broad signals at 281.0 and 223.6 ppm, respectively.

The vinylidene compounds described above represent the first reported examples of technetium–carbene complexes, and therefore, a single-crystal diffraction study of Tc(=C=CHPh)Cl(dppe)$_2$ was undertaken.[7] The complex Tc(=C=CHPh)Cl(dppe)$_2$ crystallizes from benzene/hexane solutions as orange plates. The structure (shown in Figure 1) is a distorted octahedron. The Tc–C(5) bond length at 1.861(9) Å is consistent with the assignment of a Tc=C double bond. The bond length between the α- and β-carbon atoms (C(5)–C(6)) of the terminal vinylidene ligand, at 1.265(13) Å, is in agreement with a C=C double bond, being within the range previously reported for such unsaturated carbene ligands.[1k–m] The analogous rhenium complex Re(=C=CHPh)Cl(dppe)$_2$ has also been characterized by single-crystal diffraction,[8] and the Tc=C(carbene) bond is significantly shorter than the Re=C(carbene) bond (2.046(8) Å). The Tc–C(5)–C(6) angle (173.0(8)°) is also much more linear than the Re–C(5)–C(6) (166(1)°) angle in Re(=C=CHPh)Cl(dppe)$_2$.[8]

Scheme 2



Treatment of a THF solution containing either of the terminal vinylidene complexes Tc(=C=CHR)Cl(dppe)$_2$ (R = Ph,[9] *t*-Bu[10]) with 1 equiv of acid (HBF$_4$ for R = Ph, HNMe$_3$BPh$_4$ for R = *t*-Bu) results in an instant loss of color and the formation of the respective cationic carbyne complex Tc(≡CCH$_2$R)Cl(dppe)$_2^+$ (R = Ph, *t*-Bu) (Scheme 2). The accompanying spectroscopic changes confirm the presence of a terminal carbyne ligand. For example, the $\nu_{C=C}$ band in the IR is no longer present. The β-carbon signals in the ^{13}C NMR have shifted to higher field (Ph, 14.31 ppm; *t*-Bu, 29.0 ppm), consistent with their conversion to CH$_2$ groups. The α-carbon for [Tc(≡CCH$_2$*t*-Bu)Cl(dppe)$_2$]BPh$_4$ has shifted to lower field (240.9 ppm). Unfortunately, the α-carbon in the complex [Tc(≡CCH$_2$Ph)Cl(dppe)$_2$]BF$_4$ could not be identified.[11]

The compounds Tc(≡CCH$_2$R)Cl(dppe)$_2^+$ (R = Ph, *t*-Bu) are the first examples of technetium–carbyne

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[7] Crystal data for Tc(=C=HPh)Cl(dppe)$_2$·1.5C$_6$H$_6$: orange plate; M_r = 1150.4; space group $P\bar{1}$; a = 10.175(3) Å; b = 12.807(3) Å; c = 22.735(9) Å, α = 96.09(3)°, β = 92.17(3)°, γ = 107.80(2)°; V = 2797(1) Å^3; Z = 2; d_{calc} = 1.365 g/cm^3; Siemens R3m/V diffractometer; 203 K; Mo Kα radiation (λ = 0.710 73 Å); scan method 2Θ–Θ; data collection range 4.0–45.0°; total number of data measured 7844; number of independent reflections 7319 (R_{int} = 11.37%); number of observed reflections 4522 ($F > 4.0\sigma(F)$). The structure was solved by direct methods and refined by a full-matrix least-squares procedure to give final residuals of R = 0.0555 and R_w = 0.0691; GOF = 1.10. From final difference Fourier maps, residual electron densities of 0.91 and –0.45 e/Å^3 were present.

[8] Pombeiro, A. J. L.; Almeida, S. S. P. R.; Silva, F. C. G.; Jeffrey, J. C.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1989**, 2381–2387.

[9] [Tc(≡CCH$_2$Ph)Cl(dppe)$_2$]BF$_4$: Tc(=C=CHPh)Cl(dppe)$_2$ (50 mg, 0.048 mmol) was dissolved in THF (5 mL). HBF$_4$·Et$_2$O (0.048 mmol, 30% solution in Et$_2$O) was added to this solution dropwise. The solution instantly changed from orange to colorless. Addition of hexane precipitated the product as a white solid (48 mg, 89%). The product can be further purified by recrystallization from dichloromethane/hexane at –40 °C. ^{1}H NMR (THF, 295 K): δ 6.0–7.8 (m, C$_6$*H*$_5$, 45 H), 2.92 (m, PC*H*$_2$, 4 H), 2.76 (m, PC*H*$_2$, 4 H), 2.55 (m, C*H*$_2$Ph, 2 H). ^{13}C NMR (THF-d_8, 295 K): δ 135–129 (m, Ph (dppe + vinylidene)), 30.5 (m, PCH$_2$), 14.31 (s, C—*C*H$_2$Ph). Anal. Calcd for C$_{60}$H$_{55}$BClF$_4$P$_4$Tc·CH$_2$Cl$_2$: C, 60.79; H, 4.77. Found: C, 60.58; H, 4.41.

[10] [Tc(≡CCH$_2$-*t*-Bu)Cl(dppe)$_2$]BPh$_4$: Tc(=C=CH-*t*-Bu)Cl(dppe)$_2$ (50 mg, 0.048 mmol) was dissolved in THF (5 mL), and a solution of THF containing HNMe$_3$BPh$_4$ (18 mg, 0.048 mmol) was added. The solution changed from orange-red to colorless. Addition of hexane precipitated the product as a white solid (54 mg, 82%). The product can be further purified by recrystallization from dichloromethane/hexane at –40 °C. ^{1}H NMR (CD$_2$Cl$_2$, 295 K): δ 7.5–6.6 (m, C$_6$*H*$_5$, 60 H), 2.96 (m, PC*H*$_2$, 4 H), 2.70 (m, PC*H*$_2$, 4 H), 0.90 (m, C*H*$_2$-*t*-Bu, 2 H), –0.02 (s, *t*-Bu, 9H). ^{13}C NMR (CD$_2$Cl$_2$, 295 K): δ 240.9 (b, Tc≡*C*), 164.8–162.0 (m, Ph), 136.3–122.0 (m, Ph), 33.5 (s, *C*CH$_3$), 29.4 (s, C*C*H$_3$), 29.2 (m, *C*H$_2$), 29.0 (s, *C*H$_2$Ph). Anal. Calcd for C$_{82}$H$_{79}$BClP$_4$Tc·CH$_2$Cl$_2$: C, 70.32; H, 5.76. Found C, 70.16; H, 5.14.

[11] Identifying these resonances in the complexes described here proved somewhat difficult. The α-carbon should appear as a quintet, due to coupling to the four phosphorus atoms. This type of splitting makes identification of the signal from the base line noise problematic. The difficulty in obtaining a signal for the carbene carbon is further complicated with these particular complexes by the $^9/_2$ spin of ^{99}Tc.

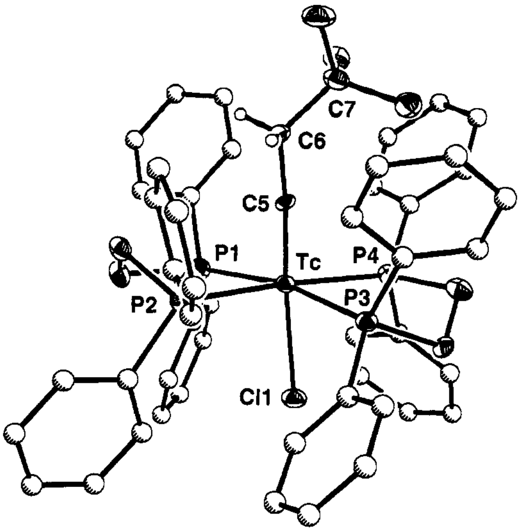

Figure 2. ORTEP representation with 50% probability ellipsoids (isotropically refined atoms are represented by shaded (carbon) or open (hydrogen) circles [BPh$_4$]$^-$ has been omitted for clarity) of [Tc(≡CCH$_2$-*t*-Bu)Cl(dppe)$_2$]$^+$. Selected bond lengths (Å) and angles (deg) are as follows: Tc–C(5) = 1.724(7), C(5)–C(6) = 1.486(10), Tc–Cl(1) = 2.523(3), Tc–P(1) = 2.538(3), Tc–P(2) = 2.487(3), Tc–P(3) = 2.453(3), Tc–P(4) = 2.491(3); Cl–Tc–C(5) = 175.9(3), Tc–C(5)–C(6) = 172.3(6), P(1)–Tc–C(5) = 94.9(3), P(2)–Tc–C(5) = 88.3(3), P(3)–Tc–C(5) = 94.3(3), P(4)–Tc–C(5) = 94.5(3).

complexes, and therefore, a single-crystal diffraction study of [Tc(≡CCH$_2$*t*-Bu)Cl(dppe)$_2$]BPh$_4$ was carried out.[12] The carbyne complex [Tc(≡CCH$_2$-*t*-Bu)Cl(dppe)$_2$]BPh$_4$ crystallizes as colorless cubes from a dichloromethane/hexane solution at -40 °C. The structure is that of a distorted octahedron. The Tc–C(5) distance of 1.724(7) Å is significantly shorter than the corresponding Tc=C(carbene) bond in Tc(=C=CHPh)Cl(dppe)$_2$ and is consistent with the assignment of Tc–C(5) as a triple bond. A closely related rhenium complex has also been reported ([Re(≡CCH$_2$-*t*-Bu)F(dppe)$_2$]BF$_4$).[13] A comparison of the two structures reveals a significantly shorter T≡C(carbyne) distance, with the Re≡C(carbyne) bond length being 1.772(7) Å. However, this variance could be due to the relative *trans* effects of the differing halide ligands. However, the technetium–carbon bond lengths (Tc=C(carbene) 1.861(9) Å and Tc≡C(carbyne) 1.724(7) Å), do not deviate significantly from the range of distances observed for other transition metals.[1,2]

The formation of vinylidene complexes by the reaction of terminal alkynes with TcCl(dppe)$_2$ is much more facile than the corresponding reactions with ReN$_2$Cl(dppe)$_2$.[8] This is probably a result of the availability of a vacant coordination site on TcCl(dppe)$_2$. The 16-electron complex TcCl(dppe)$_2$ is currently being examined with respect to its reactivity toward other small molecules.

Acknowledgment. This work was supported by the Laboratory Directed Research and Development program and the U.S. Department of Energy, Division of Chemical Sciences, Office of Basic Energy Sciences.

Supplementary Material Available: Tables of atomic coordinates, bond lengths and angles, anisotropic thermal parameters, and a summary of X-ray diffraction data for Tc(=C=CHPh)Cl(dppe)$_2$ and [Tc(≡CCH$_2$-*t*-Bu)Cl(dppe)$_2$]BPh$_4$ (21 pages). Ordering information is given on any current masthead page.

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[12] Crystal data for [Tc(≡CCH$_2$-*t*-Bu)Cl(dppe)$_2$]BPh$_4$·Ch$_2$Cl$_2$: colorless prism; $M_r = 1416.4$; space group $P2_1/c$; $a = 18.853(14)$ Å; $b = 16.151(10)$ Å; $c = 23.22(2)$ Å, $\beta = 99.38(6)°$, $V = 6977(8)$ Å^3; $Z = 4$; $d_{\mathrm{calc}} = 1.348$ g/cm^3; Siemens R3m/V diffractometer; 203 K; Mo Kα radiation ($\lambda = 0.710\,73$ Å); scan method 2Θ–Θ; data collection range 4.0–40.0°; total number of data measured 17 098; number of independent reflections 9176 ($R_{\mathrm{int}} = 8.15\%$); number of observed reflections 4887 ($F > 6.0\sigma(F)$). The structure was solved by direct methods and refined by a full-matrix least-squares procedure to give final residuals of $R = 0.0512$ and $R_w = 0.0591$; GOF = 1.20. From final difference Fourier maps, residual electron densities of 0.83 and −1.01 e/Å^3 were present.

[13] Pombeiro, A. J. L.; Hills, A.; Hughes, D. L.; Richards, R. L. *J. Organomet. Chem.* **1988**, *352*, C5–C7.