Organometallics **1993**, *12*, 2426–2428

Methyl Grignard Reactions with $\mathrm{Tc_2(NAr)_4(\mu\text{-}NAr)_2}$: The Imido Ligand as a Leaving Group

Anthony K. Burrell and Jeffrey C. Bryan*

Inorganic and Structural Chemistry Group (INC-1), Los Alamos National Laboratory, Los Alamos, New Mexico 87545

Received April 20, 1993

Summary: The reaction of 2 equiv of MeMgCl with $\mathrm{Tc_2(NAr)_4(\mu\text{-}NAr)_2}$ *(Ar = 2,6-dimethylphenyl) results in displacement of an imido ligand and the formation of* $\mathrm{TcMe_2(NAr)(\mu\text{-}NAr)_2Tc(NAr)_2}$*. Treatment of* $\mathrm{TcMe_2(NAr)(\mu\text{-}NAr)_2Tc(NAr)_2}$ *with a further 2 equiv of MeMgCl again results in the substitution of an imido ligand and the formation of* $\mathrm{Tc_2(NAr)_2(\mu\text{-}NAr)_2Me_4}$*. Single crystal X-ray determinations of these complexes confirmed the unprecedented substitution of an imido ligand by two methyl groups.*

Homoleptic imido complexes exist for only a very few transition metals.[1] In general homoleptic complexes provide an excellent opportunity to examine functional group reactivity without complications arising from ancillary ligands. To date, systematic investigations of homoleptic imido complexes are rare.[1b] Recently, we have isolated several new examples of homoleptic imido complexes (of technetium and rhenium).[1i,2] These complexes are proving to have a rich and diverse chemistry.[2] We report here the unprecedented substitution of imido ligands by methyl groups in the complex $\mathrm{Tc_2(NAr)_4(\mu\text{-}NAr)_2}$ (Ar = 2,6-dimethylphenyl).

Treatment of $\mathrm{Tc_2(NAr)_4(\mu\text{-}NAr)_2}$ with 2 equiv of MeMgCl in THF results in the red solution slowly changing to deep ruby. This new color is due to the formation of $\mathrm{TcMe_2(NAr)(\mu\text{-}NAr)_2Tc(NAr)_2}$ (Scheme I).[3] This complex is stable in air for short periods and may be purified by column chromatography. The ^{1}H NMR spectrum of $\mathrm{TcMe_2(NAr)(\mu\text{-}NAr)_2Tc(NAr)_2}$ is consistent with its formulation as a nonsymmetrical dimer. Five distinct methyl resonances, in a ratio of 1:2:1:1:1, are observed. When the NMR sample is cooled, the signal ascribed to the methyl protons of the bridging imido ligands splits into two separate signals consistent with some hindered rotation about the N–C bond.

Single crystals suitable for X-ray diffraction were obtained by the slow evaporation of a benzene:hexamethyldisiloxane solution of $\mathrm{TcMe_2(NAr)(\mu\text{-}NAr)_2Tc(NAr)_2}$. The crystallographic analysis[4] (Figure 1) confirmed the nature of the dimer. The geometry about Tc(1) may be described as a distorted square based pyramid with the terminal imido ligand occupying the apical position. The second technetium atom (Tc(2)) is more correctly described as having a distorted tetrahedral arrangement of the two bridging imido groups and two terminal imido ligands.

The nitrogen atoms of the bridging imido ligands and the technetium atoms do not lie in a single plane but exist with a "butterfly" geometry with the angle between the "wings" being 158° . The Tc–Tc distance, at 2.673(2) Å, is consistence with a d^1–d^1 single bond.[1i]

Treatment of $\mathrm{TcMe_2(NAr)(\mu\text{-}NAr)_2Tc(NAr)_2}$ with an additional 2 equiv of MeMgCl results in the substitution of a second terminal imido ligand and the formation of $\mathrm{Tc_2(NAr)_2(\mu\text{-}NAr)_2Me_4}$.[5] This tetramethyl dimer can be purified by column chromatography and crystallizes as a red/orange solid. The ^{1}H NMR spectrum for $\mathrm{Tc_2(NAr)_2(\mu\text{-}NAr)_2Me_4}$ is not as simple as might be expected. There are four resonances (in a ratio of 1:2:2:1) that may be ascribed to methyl protons. Assuming the pairs of imido ligands are related by symmetry and there is free rotation about the carbon–nitrogen bonds, only three methyl signals should be observed. Clearly, there is some hindered rotation associated with one of the pairs of imido ligands, as is seen in ^{1}H NMR spectrum of $\mathrm{TcMe_2(NAr)(\mu\text{-}NAr)_2Tc(NAr)_2}$ below room temperature. If a generally symmetrical complex is assumed for $\mathrm{Tc_2(NAr)_2(\mu\text{-}NAr)_2Me_4}$ (i.e. both technetium atoms have one terminal imido and two terminal methyl ligands and are bridged by two imido ligands), there are two possible geometric conformations. The first of these isomers has the two sets

---

[1] (a) Anhaus, J. T.; Kee, T. P.; Schofield, M. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 1642–1643. (b) Schofield, M. H.; Kee, T. P; Anhaus, J. T.; Schrock, R. R.; Johnson, K. H.; Davis, W. M. *Inorg. Chem.* **1991**, *30*, 3595–3604. (c) Danopoulos, A. A.; Wilkinson, G.; Hursthouse, M. B.; Hussain, B. *Polyhedron* **1989**, *8*, 2947–2949. (d) Danopoulos, A. A.; Leung, W.-H.; Wilkinson, G.; Hussain-Bates, B.; Hursthouse, M. B. *Polyhedron* **1990**, *9*, 2625–2634. (e) Danopoulos, A. A.; Wilkinson, G. *Polyhedron* **1990**, *9*, 1009–1010. (f) Smith, D. P.; Allen, K. D.; Carducci, M. D.; Wigley, D. E. *Inorg. Chem.* **1992**, *31*, 1319–1320. (g) Danopoulos, A. A.; Longley, C. J.; Wilkinson, G.; Hussain, B.; Hursthouse, M. B. *Polyhedron* **1989**, *8*, 2657–2670. (h) Danopoulos, A. A.; Wilkinson, G.; Hussain-Bates, B.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1991**, 269–275 and 1855–1860. (i) Burrell, A. K.; Bryan, J. C. *Angew. Chem.* **1993**, *105*, 85–86; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 94–95.

[2] $\mathrm{Tc_2(NAr)_4(\mu\text{-}NAr)_2}$ was prepared by the reduction of $\mathrm{Tc(NAr)_3I}$ with 1 equiv of sodium. Burrell, A. K; Clark, D. L.; Smith, W. H.; Sattelberger A. P.; Bryan J. C. Manuscript in preparation.

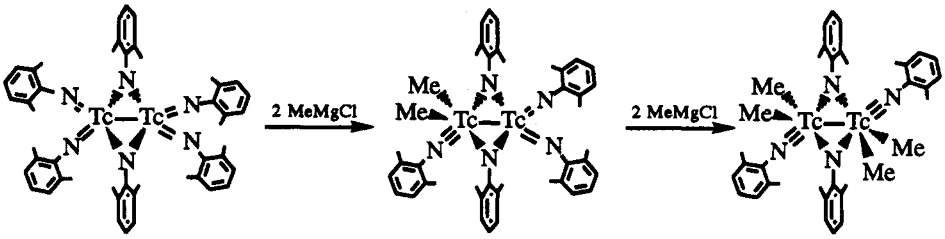
[3] $\mathrm{TcMe_2(NAr)(\mu\text{-}NAr)_2Tc(NAr)_2}$: $\mathrm{Tc_2(NAr)_4(\mu\text{-}NAr)_2}$ (50 mg, 0.05 mmol) was dissolved in THF (15 mL) and MeMgCl (0.10 mmol as a 3% solution in THF) added. The mixture was stirred for 2 h and the solvent then removed in vacuo. The residue was extracted with benzene and chromatographed on alumina. The red band was collected and the product was obtained as a red solid by the addition of $\mathrm{(Me_3Si)_2O}$ (32 mg, 72%). ^{1}H NMR ($\mathrm{C_6D_6}$, 295 K): δ 7.20–6.49 (m, $\mathrm{C_6\mathit{H}_3Me_2}$, 15 H), 2.34 (s, $\mathrm{C_6H_3C\mathit{H}_3}$, 6 H), 2.15 (s, $\mathrm{C_6H_3C\mathit{H}_3}$, 12 H), 2.13 (s, $\mathrm{C_6H_3C\mathit{H}_3}$, 6 H), 1.94 (s, $\mathrm{C\mathit{H}_3}$, 6 H), 1.48 (s, $\mathrm{C_6H_3C\mathit{H}_3}$, 6 H). Anal. Calcd for $\mathrm{C_{42}H_{51}N_5Tc_2}$: C, 61.30; H, 6.25; N, 8.51. Found: C, 61.77; H, 6.51; N, 8.07.

[4] Crystal data for $\mathrm{TcMe_2(NAr)(\mu\text{-}NAr)_2Tc(NAr)_2}$: dark red, rhombohedral, 0.25 × 0.21 × 0.36 mm; $M_r = 823.7$; space group $P\bar{1}$; $a = 10.601(3)$ Å; $b = 13.513(3)$ Å; $c = 16.030(5)$ Å, $\alpha = 78.83(2)°$, $\beta = 78.95(2)°$, $\gamma = 81.50(2)°$; $V = 2197(1)$ Å^3; $Z = 2$; $d_{\mathrm{calcd}} = 1.347$ g/cm^3; Siemens R3m/V diffractometer; 203 K; Mo Kα radiation ($\lambda = 0.710\,73$ Å); scan method 2θ–θ; data collection range 4.0–48.0°; total number of data measured 8103; number of independent reflections 7053 ($R_{\mathrm{int}} = 2.3\%$); number of observed reflections 3975 ($F > 8.0\sigma(F)$). The structure was solved by direct methods and refined by a full-matrix least-squares procedure to give final residuals of $R = 0.0872$ and $R_w = 0.1226$; GOF = 2.22. From final difference Fourier maps, residual electron densities of +2.42 and −1.43 e/Å^3 were present.

[5] $\mathrm{Tc_2(NAr)_2(\mu\text{-}NAr)_2Me_4}$: $\mathrm{TcMe_2(NAr)(\mu\text{-}NAr)_2Tc(NAr)_2}$ (50 mg, 0.06 mmol) was dissolved in THF (15 mL) and MeMgCl (0.13 mmol as a 3% solution in THF) added. The mixture was stirred for 4 h and the solvent then removed in vacuo. The residue was extracted with benzene and chromatographed on alumina. The orange band was collected and the product was obtained as a red/orange solid by the addition of $\mathrm{(Me_3Si)_2O}$ (30 mg, 68%). ^{1}H NMR ($\mathrm{C_6D_6}$, 295 K): δ 7.25–6.49 (m, $\mathrm{C_6\mathit{H}_3Me_2}$, 12 H), 2.32 (s, $\mathrm{C_6H_3C\mathit{H}_3}$, 6 H), 2.04 (s, $\mathrm{C_6H_3C\mathit{H}_3}$, 12 H), 1.93 (s, $\mathrm{C\mathit{H}_3}$, 12 H), 1.20 (s, $\mathrm{C_6H_3C\mathit{H}_3}$, 6 H). Anal. Calcd for $\mathrm{C_{36}H_{48}N_4Tc_2}$: C, 59.01; H, 6.60; N, 7.65. Found: C, 59.24; H, 6.84; N, 7.81.

0276-7333/93/2312-2426$04.00/0

Scheme I



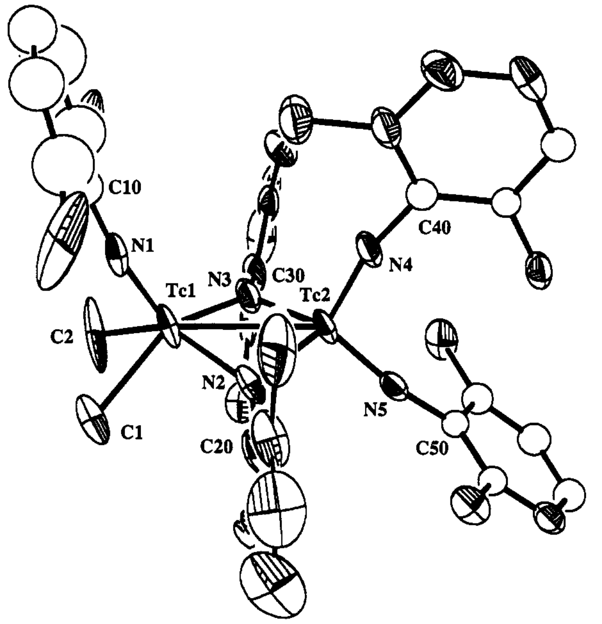
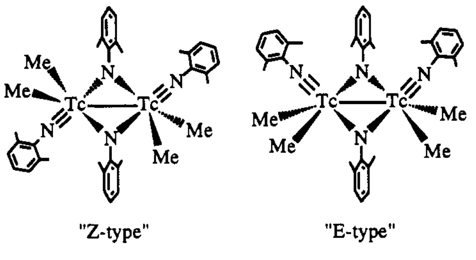


Figure 1. ORTEP representation (35% ellipsoids, isotropically refined atoms are represented by open circles) of $TcMe_2(NAr)(\mu\text{-}NAr)_2Tc(NAr)_2$. Selected bond lengths (Å) and angles (deg) are as follows: Tc(1)–Tc(2), 2.673(2); Tc(1)–N(1), 1.702(11); Tc(1)–N(2), 1.973(13); Tc(1)–N(3), 1.974(10); Tc(1)–C(1), 2.119(17); Tc(1)–C(2), 2.144(17); Tc(2)–N(2), 1.918(10); Tc(2)–N(3), 1.922(13); Tc(2)–N(4), 1.746(11); Tc(2)–N(5), 1.76(11); Tc(1)–N(1)–C(10), 170.8(9); Tc(2)–N(4)–C(40), 166.1(10); Tc(2)–N(5)–C(50), 170.3(8).

of methyl ligands on opposite sides of the Tc–N–Tc plane, the "*Z*-type" structure. The second isomer has all of the methyl ligands on the same side of the Tc–N–Tc plane, an "*E*-type" structure.



Single crystals of $Tc_2(NAr)_2(\mu\text{-}NAr)_2Me_4$ suitable for X-ray diffraction were obtained by the slow evaporation of a benzene:hexamethyldisiloxane solution. Only the *Z* isomer is observed in the solid state (Figure 2).[6] This complex is best described as an edge-bridged square based pyramidal dimer with the terminal imido ligands occupying the apical positions. Like the dimethyl dimer $TcMe_2(NAr)(\mu\text{-}NAr)_2Tc(NAr)_2$, the bridging nitrogen atoms and the technetium atoms exist as a butterfly, but with a larger (167°) angle between the wings. Also, the Tc–Tc distance (at 2.733(1) Å) is within the range expected for a d^1–d^1 dimer.[1i]

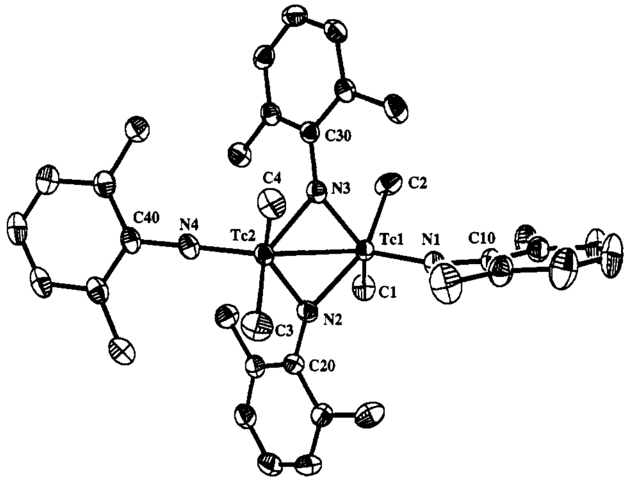
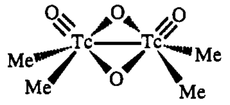


Figure 2. ORTEP representation (50% ellipsoids) of $Tc_2(NAr)_2(\mu\text{-}NAr)_2Me_4$. Selected bond lengths (Å) and angles (deg) are as follows: Tc(1)–Tc(2), 2.733(1); Tc(1)–N(1), 1.713(2); Tc(1)–N(2), 2.001(2); Tc(1)–N(3), 1.927(2); Tc(1)–C(1), 2.134(2); Tc(1)–C(2), 2.149(2); Tc(2)–N(2), 1.942(2); Tc(2)–N(3), 1.995(2); Tc(2)–N(4), 1.719(3); Tc(2)–C(3), 2.153(2); Tc(2)–C(4), 2.159(2); Tc(1)–N(1)–C(10), 164.5(2); Tc(2)–N(4)–C(40), 175.5(2).

Interestingly, the isoelectronic oxo complex $Tc_2(O)_2(\mu\text{-}O)_2(Me)_4$ was reported by Herrmann and co-workers.[7] This oxo analog was also structurally characterized and exists, at least in the solid state, as the *E*-type structure. It is possible that the *E*- and *Z*-type structures for $Tc_2(O)_2(\mu\text{-}O)_2(Me)_4$ and $Tc_2(NAr)_2(\mu\text{-}NAr)_2Me_4$ can interconvert in solution.



Substitution of imido ligands is not a new reaction. Addition of acids results in elimination of the imido and usually coordination of the conjugate base to the metal center.[8] For example, when $ReMe(NAr)_3$ is treated with 2 equiv of PhSH, one of the imido ligands is lost as H_2NAr

---

[6] Crystal data for $Tc_2(NAr)_2(\mu\text{-}NAr)_2Me_4$: dark red, shard, 0.29 × 0.37 × 0.79 mm; M_r = 734.6; space group $P\bar{1}$; a = 11.832(3) Å; b = 11.917(3) Å; c = 13.286(3) Å; α = 75.33(2)°; β = 71.10(2)° ; γ = 84.82(2)°; V = 1714(1) Å^3; Z = 2; d_{calcd} = 1.419 g/cm^3; Siemens R3m/V diffractometer; 203 K; Mo Kα radiation (γ = 0.710 73 Å); scan method 2θ–θ; data collection range 4.0–54.0°; total number of data measured 7909; number of independent reflections 7537 (R_{int} = 18.5%); number of observed reflections 6135 ($F > 4.0\sigma(F)$). The structure was solved by direct methods and refined by a full-matrix least-squares procedure to give final residuals of R = 0.0234 and R_w = 0.0335; GOF = 0.94. From final difference Fourier maps, residual electron densities of +0.34 and −0.34 e/Å^3 were present.

[7] Herrmann, W. A.; Alberto, R.; Kiprof, P.; Baumgärtner, F. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 189–191.

[8] Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; John Wiley: New York, 1988.

to give $ReMe(NAr)_2(SPh)_2$.[9] Alternatively, in certain instances imido ligands may be removed reductively. Thus, the addition of PMe_2Ph to $Os(NAr')_3$ (Ar′ = 2,6-diisopropylphenyl) reduces the osmium to give $Os(NAr')_2(PMe_2Ph)_2$ and $Ar'N{=}PMe_2Ph$.[1a] To the best of our knowledge the reactions described here are the first examples of simple substitution of an imido group by two methyl ligands. The alkylation reactions described above may be applicable for the modification of other imido complexes. We are continuing to examine the reactivity of imido complexes with Grignard reagents.[10]

Acknowledgment. This work is supported by the Laboratory Directed Research and Development program and performed under the auspices of the U.S. Department of Energy at Los Alamos National Laboratory. We also thank David L. Clark for helpful discussions.

Supplementary Material Available: Tables of atomic coordinates, bond lengths and angles, anisotropic thermal parameters, and a summary of X-ray diffraction data and fully labeled diagrams of $TcMe_2(NAr)(\mu\text{-}NAr)_2Tc(NAr)_2$ and $Tc_2(NAr)_2(\mu\text{-}NAr)_2Me_4$ (18 pages). Ordering information is given on any current masthead page.

OM930254B

---

[9] Cook, M. R.; Herrmann, W. A.; Kiprof, P.; Takacs, J. *J. Chem. Soc., Dalton Trans.* **1991**, 797–804.

[10] $Re_2(NAr)_4(\mu\text{-}NAr)_2$ reacts with MeMgCl in a similar fashion to $Tc_2(NAr)_4(\mu\text{-}NAr)_2$, giving $ReMe_2(NAr)(\mu\text{-}NAr)_2Re(NAr)_2$ and $Re_2(NAr)_2(\mu\text{-}NAr)_2Me_4$: Burrell, A. K.; Bryan, J. C.; Clark, D. L. Unpublished results.