Efficient Direct Synthesis of Tropidinyl Titanium and Zirconium Complexes by Allylic CH-Activation of 8-Methyl-8-azabicyclo[3.2.1]oct-2-ene (Tropidine)

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*Summary: A CH-activation and deprotonation of 8-methyl-8-azabicyclo[3.2.1]oct-2-ene (tropidine, **1**) occurs upon reaction with $TiCl_4$ and $ZrCl_4$ to afford the allyl complexes monotropidinyl titanium trichloride (**4**) and ditropidinyl zirconium dichloride (**7**), respectively. Tropidine (**1**) itself acts as the HCl scavenger, and the reactions are accompanied by the formation of 1 equiv of the hydrochloride **1**·HCl. The crystal structure of **4** is reported.*

Introduction

Many biologically active compounds feature the 8-azabicyclo-[3.2.1]octane (tropane) structural motif.[1] Examples from the tropane alkaloid family are the natural products atropine, scopolamine, and cocaine (Figure 1). The synthesis of transition metal complexes of tropane derivatives is therefore of much interest, since this might allow further regio- and stereoselective modification and the development of novel natural product syntheses.[2] Naturally, tropanes can bind to transition metals through the nitrogen atom;[3] however useful functionalizations at the positions 2−4 would require the coordination of these carbon atoms to a metal center. For example, the readily available bicyclic alkene **1** (tropidine) represents a suitable starting material, which may allow bonding to a transition metal via the nitrogen lone pair and the carbon−carbon double bond. To the best of our knowledge, we have reported the only example of such a bonding mode albeit via a proposed reductive elimination from a ruthenium hydride complex.[4] Removal of the allylic proton in **1** affords the tropidinyl anion (**2**), which displays separate 2σ- and 4π-electron donor sites and can thus be regarded as an analogue to the cyclopentadienyl ligand (Scheme 1). The first mono- and ditropidinyl complexes [(**2**)-$(C_5H_5)MCl_2$] (M = Ti, Zr) and [$(\mathbf{2})_2ZrCl_2$] have been reported by Bergman and co-workers[5] and been studied with regard to their use as precatalysts for olefin polymerization.[6] More recently, a few titanium complexes of the type [(**2**)$(R_3PN)TiCl_2$] (R = *t*Bu, *i*Pr) featuring a mixed tropidinyl phosphinimide ligand

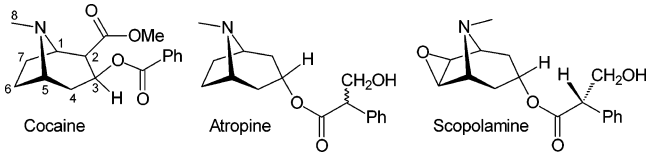
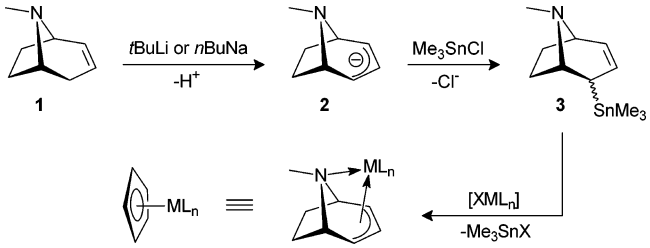


Figure 1. Tropane alkaloids.

set have been published by Stephan et al.,[7] whereas our own contribution comprises some manganese, rhenium, and ruthenium complexes.[4]

Further development of this chemistry has been hampered by the difficulty in generating **2** and its subsequent transformation into the synthetically more useful, but toxic organotin reagent **3** by transmetalation. **3** is normally obtained from tropidine (**1**) in two steps by prolonged reaction with *t*BuLi at very low temperatures for several days, followed by the reaction with Me_3SnCl.[5−7] Alternatively, shorter reaction times can be realized by the use of a Schlosser-base combination.[4] Although the stannane **3** readily reacts with metal halides to from tropidinyl complexes, the concomitant formation of toxic and volatile trimethyltin halides makes this method impractical for any large-scale industrial process (Scheme 1). In contrast, the direct use of tropidine (**1**) would establish cleaner and safer synthetic procedures and would allow this chemistry to be further exploited. We have observed that the tropidinyl titanium and zirconium complexes [(**2**)$TiCl_3$] (**4**) and [$(\mathbf{2})_2MCl_2$] (**7**) can be effectively prepared in one step by treatment of **1** with $TiCl_4$ and $ZrCl_4$, respectively.

Scheme 1



Results and Discussion

The addition of **1** to a stirred solution of 0.5 equiv of $TiCl_4$ in hexane initiated an immediate blue coloration of the reaction mixture and formation of a greenish precipitate. Evaporation of the solvent and extraction with dichloromethane afforded a

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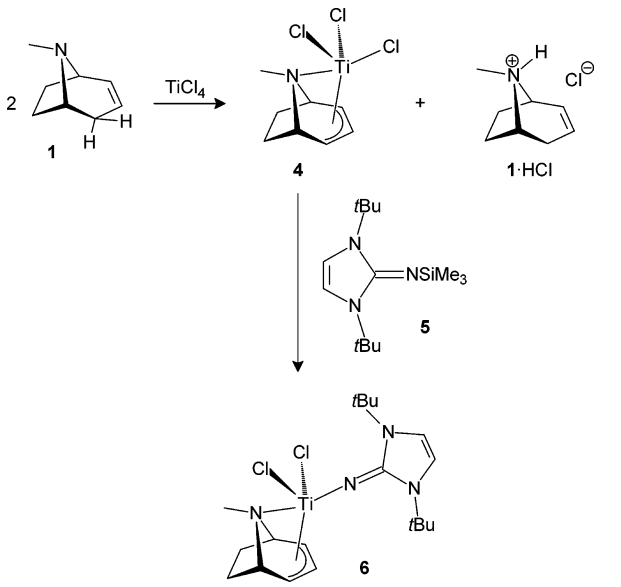
Scheme 2



blue solution, from which pure **4** could be isolated in 88% yield (based on $TiCl_4$) after filtration and crystallization (Scheme 2). The ^1H NMR spectroscopic data are in perfect agreement with those previously reported,[7] suggesting that **4** exhibits a C_s-symmetric structure in solution. Accordingly, five signals are observed in the ^{13}C NMR spectrum, with the resonances at 123.6 ppm (C3) and 111.6 ppm (C2, C4) clearly indicating the presence of an allyl ligand.[8] In addition, the yellowish precipitate separated by filtration of the CH_2Cl_2 solution could be unambiguously identified as the hydrochloride of tropidine, **1**·HCl, by means of NMR spectroscopy and elemental analysis. Two sets of resonances are observed in the ^1H and ^{13}C NMR spectra, since protonation of the nitrogen atom leads to the formation of two stereoisomers with the additional proton facing either the double bond or the CH_2CH_2 backbone of the tropidine skeleton.[9] An identical sample of **1**·HCl was obtained by addition of ethereal HCl to a solution of **1** in diethyl ether. It should also be noted that full recovery of **1** is possible by addition of sodium hydroxide to an aqueous solution of its hydrochloride and extraction with diethyl ether. In a similar manner, tropidine (**1**) is isolated after basic workup of the reaction mixture obtained by dehydration of tropine (8-methyl-8-azabicyclo[3.2.1]octan-3-ol).[4,10]

To unequivocally confirm the formation of a tropidinyl complex, single crystals of **4** were subjected to an X-ray diffraction analysis, and the molecular structure is shown in Figure 2. On first glance, the tropidinyl ligand seems to be bound symmetrically with respect to the chlorine atoms and adopts a staggered conformation with the N−CH_3 moiety bisecting the Cl1−Ti−Cl3 wedge. However, inspection of the metric parameters reveals a significant distortion, with the terminal Ti−C and allylic C−C bond distances unequal: Ti−C2 = 2.531(2) Å, Ti−C4 = 2.242(2) Å and C2−C3 = 1.363(3) Å, C3−C4 1.413(3) Å. A similar deviation has been observed for one of

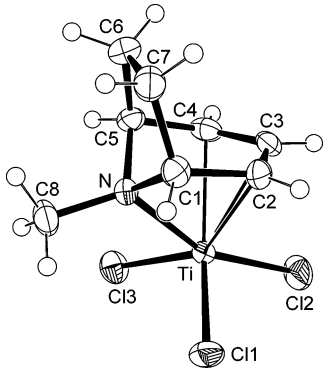


Figure 2. ORTEP plot of compound **4** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [deg]: Ti−N 2.173(2), Ti−C2 2.531(2), Ti−C3 2.361(2), Ti−C4 2.242(2), C2−C3 1.363(3), C3−C4 1.413(3); Cl1−Ti−Cl2 103.31(3), Cl1−Ti−Cl3 109.72(3), Cl2−Ti−Cl3 102.12(3), C2−C3−C4 119.5(2).

the two allyl ligands in $[(\mathbf{2})_2MCl_2]$ (**7**),[5] although most of the tropidinyl complexes that have been previously characterized by X-ray diffraction exhibit symmetrically oriented ligands.[4,6] For instance, terminal Ti−C distances of 2.394(4) and 2.377(4) Å together with allylic C−C distances of 1.375(6) and 1.374(6) Å are observed for the only other structurally characterized tropidinyl titanium complex, $[(\mathbf{2})(t\mathrm{Bu_3PN})TiCl_2]$.[7] As a result of the asymmetric binding mode of the tropidinyl ligand in **4**, the Ti−Cl distances of 2.2832(7) (Ti−Cl1), 2.2520(8) (Ti−Cl2), and 2.2607(6) Å (Ti−Cl3) also differ significantly. Furthermore, they are longer than the Ti−Cl bond lengths reported for cyclopentadienyl titanium trichlorides, e.g., Ti−Cl = 2.202−2.248 Å in $[(C_5H_5)TiCl_3]$,[11] Ti−Cl = 2.242−2.249 Å in $[(C_5Me_5)TiCl_3]$,[12] and Ti−Cl = 2.225−2.236 Å in $[(C_9H_7)TiCl_3]$ (C_9H_7 = indenyl).[13]

Complex **4** represents an ideal starting material for the synthesis of other tropidinyl titanium derivatives by chlorine substitution reactions. Since we have recently introduced a convenient and versatile route for the preparation of imidazolin-2-iminato ligands,[14−16] which represent another class of Cp-analogous ligands, we were interested in combining these ligands with the tropidinyl ligand by reacting **4** with *N*-silylated imidazolin-2-imines **5** to afford imidazolin-2-iminato complexes such as **6** (Scheme 2). The elimination of Me_3SiCl constitutes the driving force for this reaction, and complex **6** was isolated in satisfactory yield as a red solid after stirring in toluene for 48 h. The NMR data suggest that **6** adopts a C_s-symmetric structure in solution. The tropidinyl resonances are in good agreement with those observed for the closely related phosphinimido complex $[(\mathbf{2})(t\mathrm{Bu_3PN})TiCl_2]$,[7] whereas the resonances observed for the imidazoline moieties are similar to those that have been reported for cyclopentadienyl titanium dichlorides bearing imidazolin-2-iminato ligands.[16] The latter have been successfully employed in olefin polymerization catalysis,[16] and accordingly, **6** and related complexes are currently evaluated for their suitability to act as non-metallocene early transition metal polymerization catalysts.[17] In fact, **6** proved to be active

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in ethylene homopolymerization as well as ethylene/1-hexene copolymerization.[18]

The successful preparation of [(**2**)$TiCl_3$] (**4**) directly from tropidine (**1**) suggests that this reaction might be generally applicable to the preparation of transition metal tropidinyl complexes. Thus, the reaction of **1** with $ZrCl_4$ was investigated. Treatment of a suspension of $ZrCl_4$ in dichloromethane with **1** produced an instantaneous purple coloration of the reaction mixture together with the formation of a white precipitate. Attempts to isolate a monotropidinyl complex, [(**2**)$ZrCl_3$], after addition of 2 equiv of **1** failed. However, the total addition of 4 equiv resulted in the formation of an orange reaction mixture, from which the ditropidinyl complex [(**2**)$_2ZrCl_2$] (**7**) was obtained in good yield after filtration and evaporation (eq 1). **7** had been synthesized before via the stannane route (Scheme 1), and its structure determined by means of X-ray diffraction analysis.[5,6] In our hands, the spectroscopic data of the complex **7** obtained directly from tropidine (**1**) are in full agreement with those previously reported. Furthermore, characterization of the off-white solid isolated by filtration of the CH_2Cl_2 solution of **7** confirmed the formation of 2 equiv of the hydrochloride **1**·HCl based on $ZrCl_4$ (*vide supra*). The difficulty in isolating a monotropidinyl complex, [(**2**)$ZrCl_3$], is not surprising in view of other reports on the inefficiency in directly preparing monocyclopentadienyl zirconium complexes of the type [$CpZrCl_3$] from cyclopentadiene derivatives and $ZrCl_4$. Instead, such complexes are best obtained by metathesis of zirconocene dichlorides, [Cp_2ZrCl_2], and $ZrCl_4$.[19,20] Similarly, treatment of **7** with $ZrCl_4$ in dichloromethane affords a purple solution, suggesting that [(**2**)$ZrCl_3$] is formed as an intermediate during the formation **7** (eq 1).

$$ZrCl_4 + 4\ \text{equiv}\ \mathbf{1} \rightarrow \underset{\mathbf{7}}{[(\mathbf{2})ZrCl_2]} + 2\ \text{equiv}\ \mathbf{1}\cdot HCl \quad (1)$$

In summary, we have presented a facile synthesis of tropidinyl titanium and zirconium complexes, which can be conveniently prepared directly from tropidine (**1**) and $TiCl_4$ and $ZrCl_4$, respectively. This reaction does not require any additional reagents, since tropidine itself acts as a base toward its coordinated counterpart. The mechanism of formation presumably involves coordination of **1** via its nitrogen and olefinic donor moieties, whereby the interaction with the Lewis-acidic metal halides enhances the acidity of the coordinated tropidine ligand and activates the allylic C−H bond toward deprotonation. This method resembles the preparation of monocyclopentadienyl and constrained geometry titanium complexes directly from cyclopentadienes and $TiCl_4$, which can be accomplished in the presence of an additional base such as NEt_3[21,22] or even in the absence of any basic HCl scavenger.[23] It remains to be investigated if a base other than tropidine (**1**) itself can be employed; however, the ease of its reisolation from the reaction mixture would in fact not lead to a significantly more efficient protocol. In addition to their suitability to act as non-metallocene early transition metal polymerization catalysts (*vide supra*),[17] tropidinyl titanium complexes such as **4** are potentially useful reagents for synthetic applications, e.g., alkaloid synthesis, in view of the many transformations employing allyl titanium species.[24] Finally, we are currently studying the possibility of preparing various novel tropidinyl transition metal complexes in a similar fashion by direct use and CH-activation of tropidine (**1**).

Experimental Section

All operations were performed in an atmosphere of dry argon by using Schlenk and vacuum techniques. Solvents were dried by standard methods and distilled prior to use. Tropidine has been prepared by a modified procedure[4] originally published by Ladenburg.[10] The 2-(trimethylsilylimino)imidazoline **5** was prepared according to a recently published protocol.[16] Elemental analyses (C, H, N) were performed on a Elementar Vario EL elemental analyzer. ^{1}H and ^{13}C NMR spectra were measured on Jeol JNM GX 270, Jeol JNM GX 400, or Bruker DPX 400 spectrometers using the solvent as internal standard. CI-MS spectra were recorded on a Finnigan MAT 90 device.

(Tropidinyl)titanium Trichloride, [(η^3:η^1-$C_8H_{12}N$)$TiCl_3$] (4). A solution of 2.31 g (12.2 mmol) of $TiCl_4$ in 50 mL of hexane was treated dropwise over a period of 5 min with tropidine (3.0 g, 24.4 mmol, 2 equiv) at room temperature. The addition of the bicyclic amine leads to an instantaneous precipitation of a solid, which was separated by filtration after stirring for additional 15 min. The isolated green precipitate was extracted with dichloromethane to give a blue solution. After filtration, the solvent was removed *in vacuo*, yielding 2.96 (10.7 mmol, 88%) of **4** as a blue, crystalline solid. An analytically pure sample was obtained by precipitation of **4** from a dichloromethane solution using hexane. Single crystals of **4** could be isolated by slow diffusion of hexane into a solution of **1** in dichloromethane. Anal. Calcd for $C_8H_{12}Cl_3TiN$ (276.41): C, 34.76; H, 4.38; N, 5.07. Found: C, 34.98; H, 4.43; N, 5.10. ^{1}H NMR (270 MHz, toluene-d_8): δ 5.15 (t, 1H, *H*3), 4.84 (dd, 2H, *H*2+*H*4), 3.12 (m, 2H, *H*1+*H*5), 1.97 (s, 3H, N−CH_3), 1.20 (m, 4H, *H*6+*H*7). ^{13}C NMR (67.9 MHz, toluene-d_8): δ 123.6 (*C*3), 111.6 (*C*2+*C*4), 64.6 (*C*1+*C*5), 41.5 (*C*8), 33.8 (*C*6+*C*7). MS (CI, 70 eV): *m*/*z* (relative intensity) 275 (77, M^+), 240 (66, $M^+ - Cl$), 205 (13, $M^+ - 2Cl$), 122 (100, $C_8H_{12}N$).

(1,3-Di-*tert*-butylimidazolin-2-iminato)(tropidinyl)titanium Dichloride (6). 4 (0.230 g, 0.83 mmol) was dissolved in 10 mL of toluene and treated with 0.225 g (0.84 mmol) of 1,3-di-*tert*-butyl-2-(trimethylsilylimino)imidazoline (**5**) over 5 min. The solution was stirred for additional 48 h, affording a color change from blue to deep red together with the formation of a brownish precipitate. The precipitate was isolated by filtration and washed several times with hexane. Further concentration of the mother liquid *in vacuo* led to the precipitation of additional brown solid, which was isolated by filtration and washed with hexane. Following this procedure, 0.199 g (0.46 mmol, 55%) of **6** was obtained as a red-brown crystalline material. ^{1}H NMR (400 MHz, benzene-d_6): δ 5.75 (s, 2H, (NC*H*)$_2$), 5.50 (t, 1H, *H*3), 4.60 (br s, 2H, *H*2+*H*4), 3.81 (br s, 2H, *H*1+*H*5), 2.58 (s, 3H, N−CH_3) 1.82 (m, 2H, *H*6+*H*7), 1.75 (m, 2H, *H*6+*H*7), 1.51 (s, 18H, C(CH_3)$_3$). ^{13}C NMR (100 MHz, benzene-d_6): δ 128.0 (*C*3), 125.4 (*C*2+*C*4), 108.1 ((NC*H*)$_2$), 65.1 (*C*1+*C*5), 58.0 (*C*(CH$_3$)$_3$), 39.9 (*C*8), 36.0 (*C*6+*C*7), 29.0 (C(C*H*$_3$)$_3$). MS (CI, 70 eV): *m*/*z* (relative intensity) 434 (19, M^+), 377 (3, $M^+ - (CCH_3)_3$), 312 (16, $M^+ - C_8H_{12}N$), 240 (4, $M^+ - C_{11}H_{20}N_3$), 123 (16, $C_8H_{13}N$).

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Bis(tropidinyl)zirconium Dichloride (7), [(η^3:η^1-$C_8H_{12}N)_2ZrCl_2$]. $ZrCl_4$ (0.239 g, 1.03 mmol) was suspended in dichloromethane and the suspension treated dropwise with 0.560 g (4.55 mmol, 4 equiv) of tropidine (**1**) over 5 min. On addition, the suspension slowly turns violet and finally to bright orange, and a white voluminous precipitation was observed. The solution was separated from the solid, which was identified as tropidine hydrochloride, and the filtrate was evaporated to dryness, yielding 0.279 g (0.69 mmol, 67%) of **7** as an orange crystalline solid. Anal. Calcd for $C_{16}H_{24}Cl_2N_2Zr$ (406.50): C, 47.28; H, 5.95; N, 6.98. Found: C, 45.02; H, 5.76; N, 6.42. Since this compound was previously fully chraracterized,[6] no further purification was attempted. ^{1}H NMR (400 MHz, benzene-d_6): δ 5.39 (t, 2H, *H*3), 4.04 (br s, 4H, *H*2+*H*4), 3.54 (br s, 4H, *H*1+*H*5), 2.29 (s, 6H, N−CH_3), 1.86 (m, 4H, *H*6+*H*7), 1.68 (m, 4H, *H*6+*H*7). ^{13}C NMR (67.9 MHz, benzene-d_6): δ 130.9 (*C*3), 86.3 (*C*2+*C*4), 66.4 (*C*1+*C*5), 40.7 (*C*8), 38.4 (*C*6+*C*7). MS (CI, 70 eV): *m*/*z* (relative intensity) 404 (11, M^+), 389 (5, $M^+ - CH_3$), 282 (8, $M^+ - C_8H_{12}N$), 122 (98, $C_8H_{12}N$), 108 (34, 122 − CH_3).

Tropidine Hydrochloride, 1·HCl. Tropidine (0.500 g, 4.0 mmol) was dissolved in diethyl ether and subsequently treated with 3 mL of an HCl solution in diethyl ether (2 M, 6.0 mmol). Upon addition of the acid, a white precipitation was formed, which was isolated by filtration, washed with additional diethyl ether, and dried *in vacuo*. Then 0.622 g (3.9 mmol, 97%) of tropidine hydrochloride, **1**·HCl, was obtained as a white crystalline material. Anal. Calcd for $C_8H_{12}ClN$ (159.65): C, 60.18; H, 8.84; N, 8.77. Found: C, 60.05; H, 9.11; N, 8.75. ^{1}H NMR (400 MHz, dmso-d_6): δ 11.57 (br s, 1H, N*H*), 10.98 (br s, 1H, N*H*), 5.91 (m), 5.82 (m), 5.68 (m), 3.96 (q), 3.88 (t), 3.76 (br s), 2.90 (d), 2.65 (d, NCH_3), 2.63 (d, NCH_3), 2.27 (m), 2.08 (m), 1.79 (m). ^{13}C NMR (100 MHz, dmso-d_6): δ 128.2 (*C*3), 124.8 (*C*2+*C*4), 124.6 (*C*3), 124.0 (*C*2+*C*4), 61.4, 60.4, 58.6, 57.1, 38.3, 34.0, 32.7, 31.6, 30.9, 29.3, 28.0, 25.8.

Single-Crystal X-ray Structure Determination of Compound 4. $C_8H_{12}Cl_3NTi$, $M_r = 276.41$, blue fragment (0.08 × 0.20 × 0.25 mm^3), monoclinic, $P2_1/c$ (No. 14), $a = 7.0547(1)$ Å, $b = 21.9532(3)$ Å, $c = 7.6005(1)$ Å, $\beta = 109.5536(7)°$, $V = 1109.23(3)$ Å^3, $Z = 4$, $d_{calcd} = 1.655$ g cm^{-3}, $F_{000} = 560$, $\mu = 1.447$ mm^{-1}. Preliminary examination and data collection were carried out on a κ-CCD device (Nonius Mach3) with an Oxford Cryosystems cooling system at the window of a rotating anode (Nonius Fr591) with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Data collection was performed at 173 K within the θ range of $1.86° < \theta < 25.34°$. A total of 22 846 reflections were integrated. Raw data were corrected for Lorentz and polarization effects and, arising from the scaling procedure, for latent decay and absorption effects. After merging ($R_{int} = 0.039$) a sum of 2028 (all data) and 1867 [$I_o > 2\sigma(I_o)$] intensities remained and all data were used to refine 166 parameters. The structure was solved by a combination of direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were found and refined with individual isotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ and converged with R1 = 0.0260 [$I_o > 2\sigma(I_o)$], wR2 = 0.0634 (all data), GOF = 1.076, and a shift/error of <0.001. The final difference Fourier map shows no striking features ($\Delta e_{min/max} = +0.63/-0.37$ e Å^{-3}).[25]

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Supporting Information Available: Tables of crystallographic data, atomic coordinates, atomic displacement parameters, bond distances, bond angles, and a fully labeled ORTEP drawing for complex **4**. Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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