Inorg. Chem. **1998,** *37,* 6728−6730

Transition Metal Complexes of Guanidinate Dianions: Reactions between Guanidines and M(NMe$_2$)$_5$ (M = Ta, Nb)

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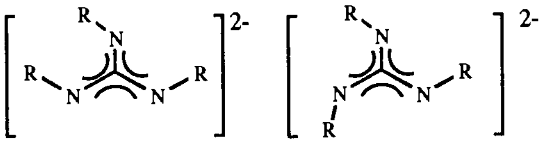
Received June 26, 1998

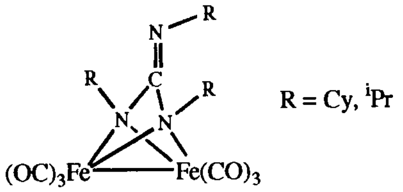
The protonation of two metal-amido groups of M(NMe$_2$)$_5$ with trialkylguanidines yielded a series of novel complexes with formulas [RNC(NR)NR]M(NMe$_2$)$_3$ (**1**−**4**) (M = Ta, Nb; R = isopropyl, cyclohexyl). These complexes contained dianionic *N,N′,N″*-trialkylguanidinate ligands which were coordinated in a chelating bidentate mode. A single-crystal X-ray study of [CyNC(NCy)NCy]Ta(NMe$_2$)$_3$ (**3**) (C$_{25}$H$_{51}$N$_6$Ta, triclinic, $P\bar{1}$, $a = 9.4155(2)$ Å, $b = 13.3188(2)$ Å, $c = 13.5215(2)$ Å, $\alpha = 117.075(1)°$, $\beta = 101.744(1)°$, $\gamma = 98.507(1)°$, $Z = 2$) confirmed the connectivity of these species. These guanidinate ligands exhibited both planarity of the central CN$_3$ group and the correct orientation of the three NR substituents to allow for π conjugation within the ligand core.

The ligating properties of monanionic guanidinates have received recent attention with a major focus being their resemblance to amidinates (Chart 1)[1]. This interest has been partly motivated by the rather limited application of guanidinates in transition metal chemistry.[2,3] We are particularly interested in the application of *N,N′,N″*-trialkylguanidines as ligands due to their ability to yield dianionic species by deprotonation of a second N−H function (Scheme 1). The resultant species could function as a diamido ligand and is isoelectronic with carbonate anion and trimethylenemethane dianions and may exhibit similar π delocalization (Y-conjugation) of the lone pairs on the sp^2 hybridized nitrogen centers (**I**).[4] In addition to their interesting electronic features, we felt that substituent modification of guanidinate dianions may allow investigation of deliberate variations to the steric and electronic parameters of the system.



I

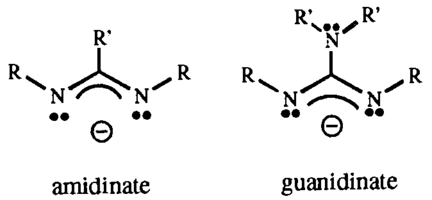
The sole reported transition metal complexes of dianionic guanidinates (**II**) were unexpected products from the reaction of Fe(CO)$_5$ and carbodiimide.[5] Recent reports of several main group complexes of guanidinate dianions include the crystallographically characterized species Li$_2$(C(NPh)$_3$),[6] Li$_2$(C(N^{t}Bu)$_3$),[7] and Sb[(^{i}PrN)$_2$CNH^{i}Pr][(^{i}PrN)$_3$C].[8]



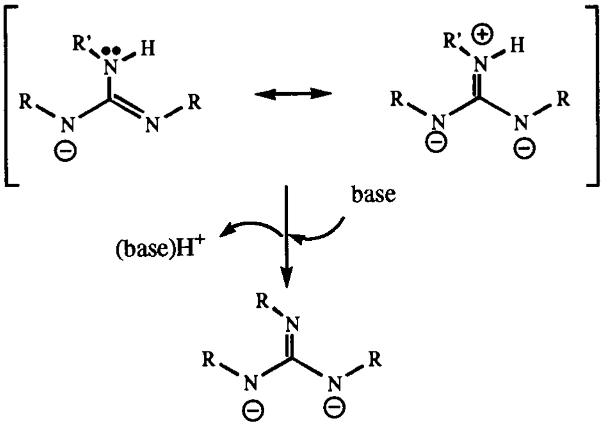
II

Our initial focus has been on high oxidation state early transition metals with the guanidine R groups restricted to alkyl in order to eliminate unanticipated resonance contributions and, through inductive effects, increase the donor ability of the ligand. The reaction of tricyclohexylguanidine or triisopropylguanidine

Chart 1



Scheme 1



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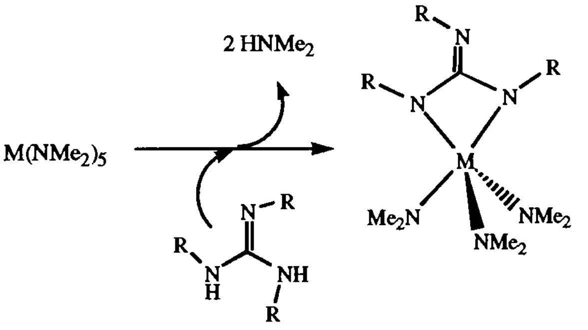
(1) (a) da S. Maia, J. R.; Gazard, P. A.; Kilner, M. Batsanova, A. S.; Howard, J. A. K. *J. Chem. Soc., Dalton Trans.* **1997**, 4625. (b) Bailey, P. J.; Mitchell, L. A.; Parsons, S. *J. Chem. Soc., Dalton Trans.* **1996**, 2839. (c) Robinson, S. D.; Sahajpal, A. *J. Chem. Soc., Dalton Trans.* **1997**, 3349. (d) Bailey, P. J.; Bone, S. F.; Mitchell, L. A.; Parsons, S., Taylor, K. J.; Yellowlees, L. J. *Inorg. Chem.* **1997**, *36*, 867. (e) Yip, H.-K.; Che, C.-M.; Zhou, Z.-Y.; Mak, T. C. W. *J. Chem. Soc., Chem. Commun.* **1992**, 1369.

(2) Chandra, G.; Jenkins, A. D.; Lappert, M. F.; Srivastava, R. C. *J. Chem. Soc. (A)* **1970**, 2250.

(3) (a) Snaith, R.; Wade, K.; Wyatt, B. K. *J. Chem. Soc. (A)* **1970**, 380. (b) Clegg, W.; Snaith, R.; Shearer, H. M. M.; Wade, K.; Whitehead, G. *J. Chem. Soc., Dalton Trans.* **1983**, 1309. (c) Pattison, I.; Wade, K*;* Wyatt, B. K. *J. Chem. Soc. (A)* **1968**, 837.

10.1021/ic980736l CCC: $15.00

with homoleptic amido complexes $M(NMe_2)_5$ (M = Ta, Nb) proceeded smoothly at room temperature, under nitrogen to provide complexes **1**−**4** in good yield (eq 1).



(1)

R	M	
^iPr	Ta	**1**
	Nb	**2**
Cy	Ta	**3**
	Nb	**4**

In all cases, the ^1H and ^{13}C NMR spectra of the products were quite similar. The alkyl proton signals shift and divide into three equal sets of resonances. This is most clear in the case of **1** and **2** where the ^iPr groups appear as three doublets of equal intensity. The integrated ratio of amido groups to guanidinate alkyls is consistent with a product having a 3:1 ratio of amido to dianionic guanidinate ligands. One of the most obvious changes in the guanidine upon deprotonation and coordination is a shift in ^{13}C NMR signals for the central, sp^2 carbon (CN_3) to the 152−158 ppm range. The corresponding resonance in the parent guanidines appear at 148.5 and 148.4 ppm for tricyclohexylguandine and triisopropylguanidine, respectively. All of the spectroscopic evidence indicated that these reactions had proceeded directly to dianionic guanidinate-containing complexes.

Final confirmation of the connectivity was provided by X-ray diffraction studies. Single crystals of **3** were subjected to X-ray analysis, which provided the results in Table 1 and displayed in Figure 1. The coordination environment of the Ta(V) center is constituted of three dimethylamido functions and an *N,N′,N″*-tricyclohexylguanidinate dianion. The overall coordination number of the Ta atom is 5 but examination of the interatomic angles indicates that the coordination geometry is better described as based on a distorted tetrahedral ligand array with the bisector of the bidentate guanidinate ligand, the Ta−C(19) vector, defining one of the vertexes. The angles formed between the Ta−C(19) vector and the three Ta−N(amido) are 105.3(4)°, 118.0(4)°, and 130.0(4)°. The angles between the three Ta−N(amido) vectors are 92.3(5)°, 93.4(5)°, and 116.1(5)°. The doubly deprotonated guanidine ligand binds to Ta through only two nitrogen atoms (N(1), N(3)) forming a planar four-membered metallacycle.

Table 1. Crystallographic Data for $Ta(NMe_2)_3[(CyN)_2C(NCy)]$ (**3**)

empirical formula	$C_{25}H_{51}N_6Ta$	
fw	616.67	
temperature	203(2) K	
wavelength	0.710 73 Å	
cryst syst	triclinic	
space group	$P\bar{1}$	
unit cell dimensions	$a = 9.4155(2)$ Å	$\alpha = 117.075(1)$ deg.
	$b = 13.3188(2)$ Å	$\beta = 101.744(1)$ deg.
	$c = 13.5215(2)$ Å	$\gamma = 98.507(1)$ deg.
volume	1420.81(4) $Å^3$	
Z	2	
density (calculated)	1.441 Mg/m^3	
absorption coefficient	3.890 mm^{-1}	
$F(000)$	632	
goodness-of-fit on F^2 [a]	1.006	
final R indices [$I > 2\sigma(I)$][a]	R1 = 0.0737, wR2 = 0.1684	
R indices (all data)[a]	R1 = 0.1039, wR2 = 0.1834	

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$. [b] $GOF = S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$: n = number of reflections, p = total number of parameters.

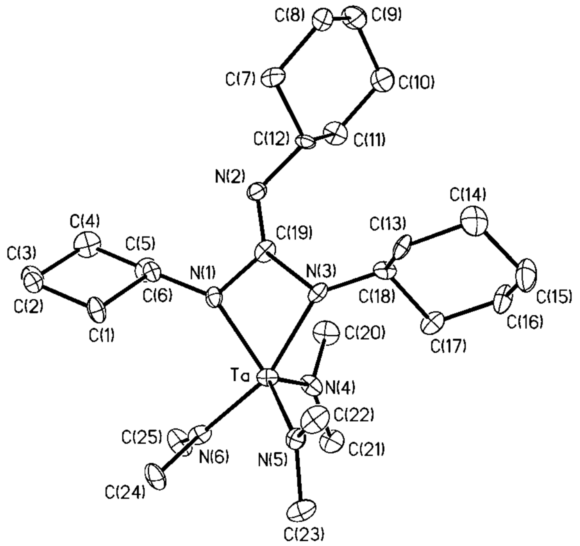


Figure 1. ORTEP diagram for $Ta(NMe_2)_3[(CyN)_2C(NCy)]$, **3**. Thermal ellipsoids are drawn at 30% probability. Selected bond distances (Å) and angles (deg): Ta−N(4), 1.963(11); Ta−N(6), 1.967(13); Ta−N(5), 1.976(11); Ta−N(1), 2.023(11); Ta−N(3), 2.120(12); Ta−C(19), 2.65(2); N(1)−C(19), 1.44(2); N(2)−C(19), 1.28(2); N(2)−C(12), 1.46(2); N(3)−C(19), 1.40(2); N(4)−Ta−N(1), 117.6(5); N(6)−Ta−N(1), 97.7(4); N(5)−Ta−N(1), 124.4(5); N(4)−Ta−N(3), 96.2(4); N(6)−Ta−N(3), 161.6(4); N(5)−Ta−N(3), 97.5(4); N(1)−Ta−N(3), 63.8(4); N(1)−Ta−C(19), 32.6(4); N(3)−Ta−C(19), 31.8(4); C(19)−N(1)−C(6), 117.1(11); C(19)−N(1)−Ta, 98.4(8); (6)−N(1)−Ta, 141.5(9); C(19)−N(2)−C(12), 125.1(12); C(19)−N(3)−C(18), 123.8(12); C(19)−N(3)−Ta, 95.5(8); C(18)−N(3)−Ta, 139.6(8); N(2)−C(19)−N(3), 137.7(14); N(2)−C(19)−N(1), 121.5(12); N(3)−C(19)−N(1), 100.6(11); N(2)−C(19)−Ta, 164.6(11).

The third guanidinate nitrogen atom, N(2), lies outside of the metal coordination sphere and based on the short C(19)−N(2) distance of 1.28(2) Å and the C(12)−N(2)-C(19) angle of 125.1(12)° is best viewed as an sp^2 hybridized, imine function. These features are consistent with negative charges of the ligand localized on the two nitrogen centers bonded to Ta. In fact, the

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(4) For some examples of heterotrimethylene methane ligands, see: (a) Seyferth, D.; Wang, T.; Davis, W. M. *Organometallics* **1994**, *13*, 4134. (b) Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 5670 (c) Ando, W.; Choi, N.; Kabe, Y. *J. Am. Chem. Soc.* **1990**, *112*, 4574. (d) Ando, W.; Yamamoto, T.; Saso, H.; Kabe, Y. *J. Am. Chem. Soc.* **1991**, *113*, 2791. (e) Kabe, Y.; Yamamoto, T.; Ando, W. *Organometallics* **1994**, *13*, 4606. (f) Jarvis, J. A. J.; Job, B. E.; Kilbourn, B. T.; Mais, R. H. B.; Owston, P. G.; Todd, P. F. *J. Chem. Soc., Chem. Commun.* **1967**, 1149. 6. (g) Armstrong, D. R.; Mulvey, R. E.; Barr, D.; Snaith, R.; Wright, D. S.; Clegg, W.; Hodgson, S. M. *J. Organomet. Chem.* **1989**, *362*, C1. (h) Ohe, K.; Ishihara, T.; Chatani, N.; Murai, S. *J. Am. Chem. Soc.* **1990**, *112*, 9646.

(5) Bremer, N. J.; Cutcliffe, A. B.; Farona, M. F.; Kofron, W. G. *J. Chem. Soc. (A)* **1971**, 3264. Bremer, N. J.; Cutcliffe, A. B.; Farona, M. F. *J. Chem. Soc., Chem. Commun.* **1970**, 932.

(6) Bailey, P. J.; Blake, A. J.; Kryszczuk, M.; Parsons, S.; Reed, D. *J. Chem. Soc., Chem. Commun.* **1995**, 1647.

(7) Chivers, T.; Parvez, M.; Schatte, G. *J. Organomet. Chem.* **1998**, *550*, 213.

(8) Bailey, P. J.; Gould, R. O.; Harmer, C. N.; Pace, S.; Steiner, A.; Wright, D. S, *Chem. Commun.* **1997**, 1161.

Ta−N(guanidine) distances (average 2.07 Å) are very close to those observed for Ta−N(amido).[9] This interpretation is in agreement with the observation of three different alkyl substituents in the ^{1}H and ^{13}C NMR spectra of **1**−**4** due to the hindered rotation of the exocylic C═N bond.

The CN_3 core (N(1), N(2), N(3), and C(19)) is planar and C(12) is coplanar with these atoms within the error of measurement (three times the estimated standard deviation). The four p orbitals for the four sp^2 centers that describe the CN_3 core are in alignment for π conjugation of the N_3C core of the guanidinate.

Despite attempts to introduce a second equivalent of guanidine through extended reaction time and increased temperature, only the reported products have so far been observed. Our future goals are to further expand the procedures of introducing guanidinate ligands, to develop general methods for the generation of dianionic guanidinate ligands, to investigate and to elucidate the chemistry of transition metal guanidinate complexes.

Experimental Section

General Considerations. All manipulations were carried out in either a nitrogen filled drybox or under nitrogen using standard Schlenk-line techniques. Solvents were distilled under nitrogen from Na/K alloy. Deuterated benzene and toluene were dried by vacuum transfer from potassium. Diisopropylcarbodiimide, dicyclohexylcarbodiimide, cyclohexylamine and isopropylamine were purchased from Aldrich and used without further purification. Preparation of $Ta(NMe_2)_5$ and $Nb(NMe_2)_5$ was carried out according to literature procedures.[10] *N*,*N′*,*N″*-tricyclohexylguanidine and *N*,*N′*,*N″*-triisopropylguanidine were prepared from the direct reaction of the appropriate carbodiimide and amine.[11] ^{1}H NMR spectra were run on a Gemini 200 MHz spectrometer with deuterated benzene or toluene as a solvent and internal standard. All elemental analyses were run on a Perkin-Elmer PE CHN 4000 elemental analysis system.

$Ta(NMe_2)_3[(CH_3)_2CHN)]_2CNCH(CH_3)_2]$ (1). A Schlenk flask was charged with $Ta(NMe_2)_5$ (1.00 g, 2.49 mmol), a stir bar and 30 mL of hexane. Triisopropylguanidine (0.46 g, 2.49 mmol) was added slowly to this solution and the reaction mixture was stirred for 24 h at room temperature. Solvent was removed from the bright yellowish solution under vacuum to yield crude **1** as a light brown solid**.** Crystallization from toluene gave 0.75 g (60%) of light yellow crystals of **1**. ^{1}H NMR (toluene-d_8, ppm) 4.92 (br m, 1H, NCH), 4.51 (br m, 1H, NCH), 4.33 (sept, 1H, NCH), 3.16(s, 18H, NCH_3), 1.41(d, 6H, CH_3), 1.32(br d, 6H, CH_3), 1.14(br d, 6H, CH_3). ^{13}C NMR (toluene-d_8, ppm) 152.03 (*C*N3), 49.62 (br, N*C*HMe$_2$), 48.72 (br, N*C*HMe$_2$) 45.65 (N*C*HMe$_2$), 45.10 (TaN*C*H$_3$), 27.51(NCH(*C*H$_3$)$_2$), 25.99 (br, NCH(*C*H$_3$)$_2$), 24.89 (br, NCH(*C*H$_3$)$_2$). Anal. Calcd for $C_{16}H_{41}N_6Ta$: C, 38.55; H, 8.29; N, 16.86. Found: C, 38.50; H, 7.91; N, 16.40.

$Nb(NMe_2)_3[(CH_3)_2CHN)]_2CNCH(CH_3)_2]$ (2). A Schlenk flask was charged with $Nb(NMe_2)_5$ (1.00 g, 3.19 mmol), a stir bar and 30 mL of hexane. Triisopropylguanidine (0.592 g, 3.19 mmol) was added slowly to this solution to give a bright orange solution. The reaction mixture was stirred overnight at room temperature. The solvent was removed under vacuum and the residue was crystallized at −30 °C from bis(trimethylsilyl) ether to give 0.35 g of microcrystalline **2** (26% yield). ^{1}H NMR (C_6D_6, ppm) 4.91 (br m, 1H), 4.78 (br m, 1H, CH), 4.35 (br m, 1H, CH), 3.01 (s, 18H, NCH_3), 1.49 (d, 6H, CH_3), 1.39 (br d, 6H, CH_3), 1.15 (br d, 6H, CH_3). ^{13}CNMR (C_6D_6 ppm) 155.2 (*C*N3), 50.98 (br, N*C*HMe$_2$), 49.96 (br, N*C*HMe$_2$), 46.37 (TaN*C*H$_3$), 45.77 (N*C*HMe$_2$), 27.34(NCH(*C*H$_3$)$_2$), 25.74 (br, NCH(*C*H$_3$)$_2$), 24.68 (br, NCH(*C*H$_3$)$_2$). Anal. Calcd for $C_{16}H_{41}N_6Nb$: C, 46.82; H, 10.07; N, 20.48. Found: C, 47.00; H, 10.17; N, 20.84.

$Ta(NMe_2)_3[(CyN)_2C(NCy)]$ (3). A Schlenk flask was charged with $Ta(NMe_2)_5$ (1.00 g, 2.49 mmol), a stir bar and 30 mL of hexane. Tricylohexylguanidine (0.76 g, 2.49 mmol) was added slowly to this solution and the reaction mixture was stirred for 24 h at room temperature. Solvent was removed from the yellowish solution under vacuum to yield crude **3.** Crystallization from bis(trimethylsilyl) ether gave 1.01 g (65%) of slightly yellow crystals of **3**. ^{1}H NMR (C_6D_6, ppm) 4.52 (br m, 1H, C*H*), 4.10 (br m, 1H, C*H*), 3.95 (br m, 1H, C*H*), 3.14 (s, 18H, NCH_3), 1.2−2.2 (br m, 30H, C_6H_{11}). ^{13}C NMR (C_6D_6,-ppm) 152.01(s, *C*N$_3$), 57.9, 54.28 (s, *2:1*, N*C*H), 45.14 (N*C*H$_3$), 37.91, 35.36, 26.98, 26.61, 25.76 (5 s, C_6H_{11}). Anal. Calcd for $C_{25}H_{51}N_6Ta$: C, 48.69; H, 8.34; N, 13.63. Found: C, 49.04; H, 8.74; N, 13.01.

$Nb(NMe_2)_3[CyN)_2C(NCy)]$ (4). A Schlenk flask was charged with $Nb(NMe_2)_5$ (1.00 g, 3.19 mmol), a stir bar and 30 mL of hexane. Tricyclohexylguanidine (0.977 g, 3.20 mmol) was added slowly to this solution to give a blood red solution. The reaction mixture was stirred for 36 h at room temperature. The solvent was removed under vacuum to yield crude **4** (0.61 g) which was extracted with diethyl ether. Crystallization at −30 °C in bis(trimethylsilyl)ether gave microcrystalline **4** in 25% yield. ^{1}H NMR (C_6D_6, ppm) 4.5−3.9 (br m, 3H, CH), 3.07 (s, NCH_3 ,18H) 2.2−1.12 (br, 30H, C_6H_{11}). ^{13}CNMR (C_6D_6, ppm) 158.23 (*C*N3), 65.86, 56.10 (s, N*C*H), 46.93 (N*C*H$_3$), 38.60, 37.80, 35.91, 26.65, 26.53, 23.02 (6s, C_6H_{11}). Anal. Calcd for $C_{25}H_{51}N_6Nb$: C, 56.80; H, 9.72; N, 15.90. Found: C, 56.52; H, 9.80; N, 15.71.

Structural Determination of 3. Despite repeated attempts at recrystallization, crystals are deposited from solution as multiple clumps. A single crystal (0.10 × 0.10 × 0.06 mm) was sectioned from a larger clump, mounted on a thin glass fiber using viscous oil, and cooled to the data collection temperature. Data were collected on a Bruker AX SMART 1k CCD diffractometer using 0.3° ω scans at 0°, 90°, and 180° in ϕ. Unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semiempirical absorption corrections based on equivalent reflections were applied (R. Blessing, *Acta Crystallogr.* **1995**, *A51*, 33−38) (reflections collected = 9879, independent reflections = 4190).

No symmetry higher than triclinic was evident from the diffraction data. Solution in $P\bar{1}$ yielded chemically reasonable and computationally stable results of refinement. The structure was solved by direct methods, completed with difference Fourier syntheses and refined with full-matrix least-squares procedures based on F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. All scattering factors and anomalous dispersion factors are contained in the SHELXTL 5.1 program library (Sheldrick, 1997, Madison, WI).

Acknowledgment. This work was supported by the Natural Sciences and Engineering Research Council of Canada.

Supporting Information Available: An X-ray crystallographic file, in CIF format, for the structure of compound **3** is available on the Internet. Access information is given on any current masthead page.

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[9] Chisholm, M. H.; Tan, L.-S.; Huffman, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 4879.

[10] Bradley, D. C.; Thomas, I. M. *Can. J. Chem.* **1962**, *40*, 1355. Bradley, D. C.; Thomas, I. M. *Can. J. Chem.* **1962**, *40*, 449.

[11] Tin, M. K. T.; Richeson, D. S. Unpublished results.