Cleavage of Titanium Dimethylamides with Methyl Iodide

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Summary: A procedure for converting metal dimethylamido complexes into the corresponding metal iodide complexes is described. Treatment of $(Me_2N)_2Ti(NRAr)_2$ ($R = C(CD_3)_2CH_3$, $Ar = 3,5\text{-}C_6H_3Me_2$) with excess methyl iodide gave $I_2Ti(NRAr)_2$ in 60% isolated yield.

We are currently examining the attributes of deuterated *N-tert*-butylanilides as ancillary ligands for paramagnetic complexes.[1] In connection with these studies we require some mixed *N-tert*-butylanilido halide complexes of titanium, which promise to be versatile starting materials. The pseudotetrahedral monochloro complex $ClTi(NRAr)_3$ ($R = C(CD_3)_2CH_3$, $Ar = 3,5\text{-}C_6H_3Me_2$; Figure 1)[2] was easily prepared by the standard route[3] involving treatment of $TiCl_4(THF)_2$[4] with 3 equiv of the monoetherate of Li(NRAr),[5] but the synthesis of $Cl_2Ti(NRAr)_2$ along similar lines gave unacceptably low yields.

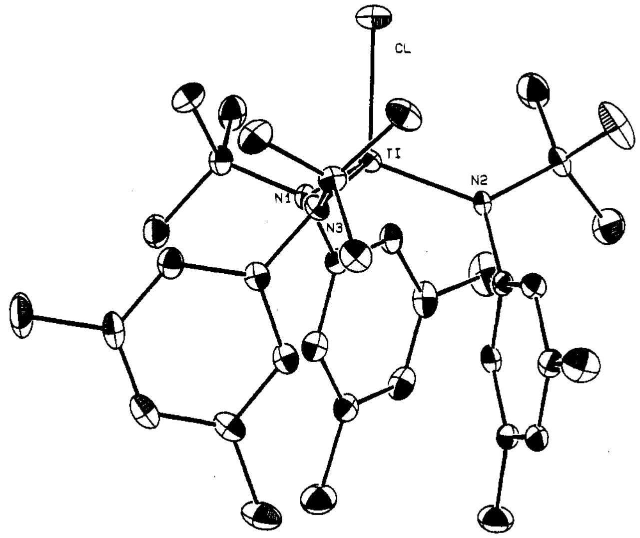
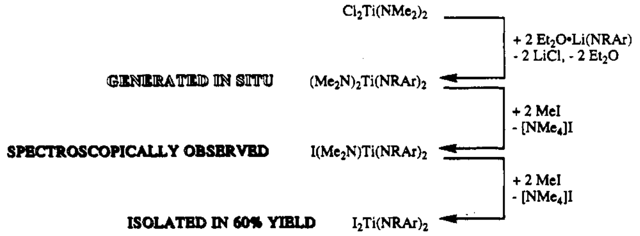


Figure 1. ORTEP drawing of the molecular structure of $ClTi(NRAr)_3$ with ellipsoids at the 35% probability level.[2] Selected bond distances: Ti–Cl, 2.281(2) Å; Ti–N(1), 1.929(4) Å; Ti–N(2), 1.922(4) Å; Ti–N(3), 1.932(4) Å. Selected bond angles: Cl–Ti–N(1), 110.4(1)°; Cl–Ti–N(2), 109.3(1)°; Cl–Ti–N(3), 110.0(1)°; N(1)–Ti–N(2), 108.8(2)°; N(2)–Ti–N(3), 111.3(2)°; N(3)–Ti–N(1), 107.0(2)°.

Scheme 1



It seemed to us that the best way to affix exactly two *N-tert*-butylanilido groups to titanium, with $Et_2O\cdot Li(NRAr)$[5] as the transfer agent, would be to utilize a titanium reactant bearing exactly two leaving groups. Such a complex is $Cl_2Ti(NMe_2)_2$,[6] which is easily prepared via the conproportionation reaction between $Ti(NMe_2)_4$ and $TiCl_4$. As anticipated, the reaction between $Cl_2Ti(NMe_2)_2$ and 2 equiv of $Et_2O\cdot Li(NRAr)$ proceeded without any significant side reactions. The product, waxy yellow $(Me_2N)_2Ti(NRAr)_2$, is exceedingly soluble in alkane solvents and therefore difficult to purify by crystallization. This is not an issue, however, because treatment of $(Me_2N)_2Ti(NRAr)_2$ (generated in situ) with excess methyl iodide gives $I_2Ti(NRAr)_2$ directly. The diiodide complex crystallizes readily.

The steps involved in the transformation of $Cl_2Ti(NMe_2)_2$ into the desired $I_2Ti(NRAr)_2$ are summarized in Scheme 1. Subsequent to the generation of $(Me_2N)_2Ti(NRAr)_2$, methylation of a dimethylamido ligand converts the latter into trimethylamine, a good leaving group. Under the reaction conditions (excess methyl iodide), trimethylamine is quaternized and $[NMe_4]I$ precipitates. The intermediate expected after cleavage of the first dimeth-

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(1) Deuteron NMR lines are narrower than corresponding proton NMR lines for paramagnetic complexes: La Mar, G. N.; Horrocks, W. D., Jr.; Holm, R. H. *NMR of Paramagnetic Molecules*; Academic Press: New York, 1973.

(2) X-ray structure of $ClTi(NRAr)_3$: A large crystal of $ClTi(NRAr)_3$ was grown by evaporation of an ether solution. A suitable trapezoidal crystal of approximate dimensions 0.30 × 0.15 × 0.30 mm³ was cut from the larger crystal and mounted on a glass fiber in a stream of cold N_2. Data were collected at −72 °C on a Rigaku AFC6R diffractometer with graphite-monochromated Mo Kα radiation. A total of 6892 reflections were collected to a 2θ value of 54.7°, of which 6630 were unique ($R_{int} = 0.150$); equivalent reflections were merged. The structure was solved by direct methods. Non-hydrogen atoms were refined anisotropically. The final cycle of least-squares refinement was based on 3520 observed reflections ($I > 3.00\sigma(I)$) and 371 variable parameters and converged (largest parameter shift was 0.01 times its esd) with $R = 0.058$ and $R_w = 0.058$. A final difference Fourier map showed no chemically significant features. Crystal data: $a = 18.119(6)$ Å, $b = 10.917(4)$ Å, $c = 19.123(7)$ Å, $\beta = 111.25(2)°$, $V = 3526(2)$ Å³, space group $P2_1/a$ (No. 14), $Z = 4$, mol wt = 630.29, ρ(calcd) = 1.153 g/cm³. Fractional coordinates are given in Table 2. Tables of bond lengths and angles are supplied as supplementary material.

(3) (a) For the synthesis of $ClTi[N(SiMe_3)_2]_3$ see: Airoldi, C.; Bradley, D. C. *Inorg. Nucl. Chem. Lett.* **1975,** *11,* 155. (b) For the synthesis of $Cl_2Ti[N(SiMe_3)_2]_2$ see: Planalp, R. P.; Andersen, R. A.; Zalkin, A. *Organometallics* **1983,** *2,* 16.

(4) Manzer, L. E. *Inorg. Synth.* **1982,** *21,* 135.

(5) For the synthesis of *N-tert*-butylaniline see: Hunter, D. H.; Racok, J. S.; Rey, A. W.; Ponce, Y. Z. *J. Org. Chem.* **1988,** *53,* 1278. Our aniline HNRAr ($R = C(CD_3)_2CH_3$, $Ar = 3,5\text{-}C_6H_3Me_2$) was prepared similarly, substituting 3,5-dimethylaniline for aniline and acetone-d_6 for acetone. The lithium salt $Et_2O\cdot Li(NRAr)$ was prepared by treatment of HNRAr with *n*-butyllithium in hexane, followed by crystallization from ether/hexane.

(6) Benzing, E.; Kornicker, W. *Chem. Ber.* **1961,** *94,* 2263.

0276-7333/94/2313-2907$04.50/0

Table 1. Physical Properties and Spectroscopic Data

	$ClTi(NRAr)_3$	$I_2Ti(NRAr)_2$
appearance	orange crystalline solid	brown-black crystalline solid
mp, °C	195–197 dec	95 dec
elemental anal., %: calcd (found)	C:68.60(68.65)	C:43.26(43.24)
	H:8.64(8.74)	H:5.45(5.60)
	N:6.67(6.44)	N:4.20(4.13)
EIMS (low resolution): $M^{•+}$ calcd (found), % of base	629.5 (629.5), 4	666.1 (666.2), 5
^1H NMR	6.76 (s, 3H, aryl para)[a]	7.07 (s, 4H, aryl ortho)[b]
	6.14 (broad, 6H, aryl ortho)	6.87 (s, 2H, aryl para)
	2.23 (s, 18H, $ArC\mathit{H}_3$)	2.11 (s, 12H, $ArC\mathit{H}_3$)
	1.16 (s, 9H, $NC(CD_3)_2C\mathit{H}_3$	1.39 (s, 6H, $NC(CD_3)_2C\mathit{H}_3$)
^2H NMR[c]	1.31 (s, $NC(C\mathit{D}_3)_2CH_3$)	1.31 (s, $NC(C\mathit{D}_3)_2CH_3$)
^{13}C NMR	150.85 (s, aryl ipso)[a,d]	138.69 (aryl)[b,e]
	136.22 (q, aryl meta)	133.97 (aryl)
	127.04 (d, aryl ortho)	132.13 (aryl)
	126.53 (d, aryl para)	130.90 (aryl)
	62.36 (s, $N\mathit{C}(CD_3)_2CH_3$)	67.56 ($N\mathit{C}(CD_3)_2CH_3$)
	30.45 (q, $NC(CD_3)_2\mathit{C}H_3$)	29.88 ($NC(CD_3)_2\mathit{C}H_3$)
	29.67 (m, $NC(\mathit{C}D_3)_2CH_3$)	29.31 (m, $NC(\mathit{C}D_3)_2CH_3$)
	21.45 (q, $Ar\mathit{C}H_3$)	21.31 ($Ar\mathit{C}H_3$)

[a] In $CDCl_3$. [b] In C_6D_6. [c] In C_6H_6 with external C_6D_6 = 7.15 ppm. [d] Gated decoupled. [e] Broad band decoupled.

ylamido ligand is the monoiodide $I(Me_2N)Ti(NRAr)_2$. Monitoring the reaction progress by ^1H NMR indicates that the monoiodide complex does in fact attain high concentrations, such that this intermediate may prove to be isolable. (One should expect methylation of $(Me_2N)_2Ti(NRAr)_2$ to be significantly more facile than methylation of $I(Me_2N)Ti(NRAr)_2$ on electronic grounds.) Cleavage of the remaining dimethylamido ligand to yield $I_2Ti(NRAr)_2$ occurs smoothly.[7]

The problem we faced in synthesizing $I_2Ti(NRAr)_2$ was to discriminate between the two different types of nitrogen donor ligands present in $(Me_2N)_2Ti(NRAr)_2$. This would be very difficult to do using hydrogen iodide because the $Ti(NRAr)_2$ portion of the molecule is sensitive to strong Brønsted acids. Use of the much milder electrophile, methyl iodide, afforded the desired selectivity. We suspect that the methodology reported here will be useful in bringing up a wide variety of starting materials from the wealth of known dimethylamido complexes of the transition metals.[8]

Experimental Section

All manipulations were carried out in an inert atmosphere using standard Schlenk techniques or a Vacuum Atmospheres drybox. Solvents were dried and degassed appropriately prior to use.

$ClTi(NRAr)_3$. $TiCl_4(THF)_2$ (0.808 g, 2.42 mmol) was added to a pale yellow solution of $Et_2O·Li(NRAr)$ (1.91 g, 7.25 mmol) in hexane (50 mL). After 48 h of stirring at ca. 30 °C, the orange-brown reaction mixture was filtered to remove LiCl. Removal of hexane in vacuo left crude $ClTi(NRAr)_3$ as an orange solid (1.24 g, 1.98 mmol, 81%), which was nearly pure as judged by ^1H NMR. Subsequent crystallization from hexane gave pure $ClTi(NRAr)_3$ (0.95 g, 1.5 mmol, 62%) in three crops. See Table 1 for physical properties and spectroscopic data and Figure 1 for an ORTEP drawing of the molecular structure.

Table 2. Positional Parameters for $ClTi(NRAr)_3$

atom	*x*	*y*	*z*
Ti	0.05486(5)	0.09997(8)	0.79039(5)
Cl	0.05114(9)	0.2928(1)	0.83484(9)
N(1)	0.0840(2)	0.1055(4)	0.7029(2)
N(2)	0.1320(2)	0.0043(4)	0.8666(2)
N(3)	−0.0489(2)	0.0260(4)	0.7598(2)
C(1)	0.0526(3)	0.1945(5)	0.6380(3)
C(2)	0.0217(3)	0.1262(5)	0.5635(3)
C(3)	0.1200(3)	0.2814(5)	0.6387(3)
C(4)	−0.0146(3)	0.2722(5)	0.6461(3)
C(5)	0.2080(3)	0.0444(5)	0.9293(3)
C(6)	0.2341(4)	0.1699(5)	0.9122(3)
C(7)	0.2753(3)	−0.0453(6)	0.9379(4)
C(8)	0.1946(4)	0.0519(6)	1.0028(3)
C(9)	−0.1050(3)	0.0299(5)	0.8037(3)
C(10)	−0.1293(3)	−0.0999(5)	0.8158(3)
C(11)	−0.1782(3)	0.1057(5)	0.7627(3)
C(12)	−0.0620(3)	0.0912(6)	0.8796(3)
C(13)	0.1449(3)	0.0234(4)	0.6966(3)
C(14)	0.1240(3)	−0.0873(5)	0.6573(3)
C(15)	0.1828(3)	−0.1660(5)	0.6514(3)
C(16)	0.2618(3)	−0.1340(5)	0.6873(3)
C(17)	0.2836(3)	−0.0252(5)	0.7267(3)
C(18)	0.2246(3)	0.0541(5)	0.7297(3)
C(19)	0.1149(3)	−0.1253(4)	0.8716(3)
C(20)	0.0737(3)	−0.1661(5)	0.9165(3)
C(21)	0.0554(3)	−0.2898(5)	0.9191(3)
C(22)	0.0793(3)	−0.3730(4)	0.8761(3)
C(23)	0.1221(3)	−0.3346(5)	0.8317(3)
C(24)	0.1393(3)	−0.2105(5)	0.8299(3)
C(25)	−0.0813(3)	−0.0435(5)	0.6910(3)
C(26)	−0.0538(3)	−0.1619(5)	0.6878(3)
C(27)	−0.0832(3)	−0.2324(5)	0.6222(3)
C(28)	−0.1404(3)	−0.1827(5)	0.5601(3)
C(29)	−0.1697(3)	−0.0649(5)	0.5615(3)
C(30)	−0.1392(3)	0.0041(5)	0.6272(3)
C(31)	0.3699(3)	0.0079(6)	0.7653(4)
C(32)	0.1603(4)	−0.2827(5)	0.6062(3)
C(33)	0.0090(4)	−0.3322(5)	0.9667(3)
C(34)	0.1486(3)	−0.4276(5)	0.7871(3)
C(35)	−0.0538(4)	−0.3612(5)	0.6200(4)
C(36)	−0.2324(4)	−0.0120(6)	0.4923(3)

$I_2Ti(NRAr)_2$. $Et_2O·Li(NRAr)$ (1.02 g, 3.88 mmol) was added all at once to a stirred slurry of $Cl_2Ti(NMe_2)_2$ (0.40 g, 2.0 mmol) in ether (10 mL) at −35 °C. After being stirred overnight at ca. 30 °C, the reaction mixture was filtered to remove LiCl. Methyl iodide (6.78 g, 47.7 mmol, 24 equiv) was then added to the dark yellow solution, and a white precipitate ($[NMe_4]I$) began to form immediately. The reaction was monitored by ^1H NMR and judged to be complete after 43 h. Ether and the excess methyl iodide were removed in vacuo, the solid residue was extracted with pentane (10 mL), and the pentane extract was filtered. The white solid was extracted with additional pentane (10 mL), and the combined pentane extracts were stored at −35 °C for 24 h to

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(7) (a) For conversion of $M_2(NMe_2)_6$ (M = Mo, W) into $M_2(NMe_2)_5I$ using Me_3SiI see: Schulz, H.; Folting, K.; Huffman, J. C.; Streib, W. E.; Chisholm, M. H. *Inorg. Chem.* **1993**, *32*, 6056. (b) For conversion of Me_2AsNMe_2 into Me_2AsI using methyl iodide see: Kober, F. *Z. Anorg. Allg. Chem.* **1973**, *401*, 243.

(8) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. *Metal and Metalloid Amides*: Ellis Horwood Limited: Chichester, U.K., 1980.

give $I_2Ti(NRAr)_2$ as a brown-black crystalline solid (0.78 g, 1.2 mmol, 60%). See Table 1 for physical properties and spectroscopic data.

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Supplementary Material Available: Tables of experimental details, bond lengths and angles, hydrogen fractional coordinates, anisotropic thermal parameters, and torsion or conformation details and a fully labeled ORTEP diagram (16 pages). Ordering information is given on any current masthead page.

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