is also important. The electrocatalytic reduction at copper gives higher yields of substituted anilines for these compounds than at electrodes which exhibit conventional electron transfer. Copper-promoted formation of surface-bound arenium ions or electrocatalytic reduction of the hydroxylamine is postulated.

Experimental Section

Coulometry and Preparative Electrolyses. A flange-type cell is designed similarly to that described by Goodridge and King.[34] Each of the two compartments has a nominal volume of 25 mL when separated by a membrane with a gasket on each side. The design includes a Luggin capillary for potentiostatic electrolyses. Three 14/20 ₸ joints on each compartment allow for electrode connection, condensor placement, and sample withdrawal. The membrane (Nafion 324) is supported between Viton gaskets to expose an area of 6 cm^2. The electrode to electrode separation is 2.5 cm. Mass transport is accomplished by nitrogen sparge through a glass frit in the bottom of the cell.

Voltammetry. A single-compartment beaker-type cell is used. All operations are performed under nitrogen. Potentials are reported vs a sodium chloride saturated calomel electrode (SSCE).

Analytical. Liquid chromatography with a Hewlett-Packard 1090 allows simultaneous determination of the UV–vis spectrum of the electrolytic products for comparison with authentic spectra. Retention time and spectral matches yield high confidence levels in structural assignment. Quantitation is via response factor obtained from authentic anilines.

Typical Electrolysis Procedure. The cathode is a 6.3 cm^2 flag of 99.9% Cu and the anode is a Ni-200 alloy expanded-metal flag of equal area. The anolyte and catholyte are separated by the cation-exchange membrane of equal exposed area. The catholyte is composed of 1 g of 3-nitro-4-hydroxybenzoic acid dissolved in 20 mL of 1 N NaOH. The anolyte consists of 25 mL of 5 N NaOH. The temperature is controlled at 25 (±1) °C. A constant current of 0.500 A (79.4 mA/cm^2) is applied after deoxygenation. Nitrogen sparge is continuous throughout the electrolysis for mass transport. The reaction is followed via liquid chromatography. The chemical yield, current efficiency, and conversion are calculated with a correction for the small (but linear) increase in catholyte volume with charge passed.

Acknowledgment. We express our appreciation to Z. Lysenko for helpful discussions.

Registry No. **1a**, 616-82-0; **1b**, 1571-72-8; **2a**, 619-14-7; **2b**, 2374-03-0; **3a**, 96-97-9; **3b**, 89-57-6; **4a**, 88-75-5; **4b**, 95-55-6; **5a**, 100-02-7; **5b**, 123-30-8; **6a**, 554-84-7; **6b**, 591-27-5; **7a**, 552-16-9; **7b**, 118-92-3; **8a**, 62-23-7; **8b**, 150-13-0; **9a**, 121-92-6; **9b**, 99-05-8; **10a**, 91-23-6; **10b**, 90-04-0; **11a**, 100-17-4; **11b**, 104-94-9; **12a**, 555-03-3; **12b**, 536-90-3; **13a**, 119-33-5; **13b**, 95-84-1; **14a**, 5460-31-1; **14b**, 53222-92-7; **15a**, 2581-34-2; **15b**, 2835-99-6; **16a**, 700-38-9; **16b**, 2835-98-5; **17a**, 4920-77-8; **17b**, 2835-97-4; **18a**, 100-29-8; **18b**, 156-43-4; **19a**, 98-95-3; **19b**, 62-53-3; **20a**, 88-73-3; **20b**, 95-51-2; **21a**, 100-00-5; **21b**, 106-47-8; **22a**, 99-99-0; **22b**, 106-49-0; **23a**, 138-42-1; **23b**, 121-57-3; Cu, 7440-50-8; C, 7440-44-0; NaOH, 1310-73-2; Cu_2O, 1317-39-1; CuO, 1317-38-0; $Cu(OH)_2$, 20427-59-2.

Reactions of Amides with Potassium Permanganate in Neutral Aqueous Solution

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Oxidation reactions of organic compounds by $KMnO_4$ are widely used in organic synthesis. Indeed, numerous examples and reviews of the reaction have been reported in the literature.[1,2] In the course of preparation of several aminobenzoic acid derivatives, we attempted to oxidize N-acetylated or N-benzoylated toluidines and xylidines with $KMnO_4$ to the corresponding carboxylic acid derivatives. The stoichiometry of the reaction shows a 1:2 molar reaction of the substrate and $KMnO_4$ (eq 1).[3] However,

$$RCH_3 + 2KMnO_4 \rightarrow RCOOK + 2MnO_2 + KOH + H_2O \quad (1)$$

to our surprise, the reaction did not go to completion when the ratio of 1:2 was employed. Instead, significant recovery of the toluidides was observed in all cases. On the other hand, the oxidizing agent seemed to be consumed completely. This puzzling observation led us to investigate systematically the oxidation reaction of toluidines and xylidines by $KMnO_4$.

Table I. Results of Oxidation Reaction of Toluidides 2 and 3 by $KMnO_4$[a]

substrate	product	yield of product,[b] %	mp, °C	lit. mp, °C	recovery of substrate,[b] %
2a	**4a**	35	177–179	181[13,17]	50
2b	**4b**	30	255–256	252–253[13,17]	60
2c	**4c**	40	286–287	278[13,17]	50
2d	**4d**	30	283–283	–	55
2e	**4e**	35	193–196	221–222 dec[8]	55
3a	**5a**	60	186–187	185[13,17]	30
3b	**5b**	35	241–243	248,[13] 248–250[17]	40
3c	**5c**	70	257–259	250,[13] 256.5[17]	20
3d	**5d**	25	269–271	270[14]	60
3e	**5e**	20	210 dec	216–217 dec,[8] 208[14]	60

[a] Substrate: $KMnO_4$ = 1:4 by mole; reflux for 1.5 h. [b] The yields are average values of at least three runs.

Results and Discussion

Although there are countless reports on the subject of oxidation of $KMnO_4$, only a few examples of reaction with N-acylated toluidines (**2** and **3**) can be found in the literature. *p*-Acetotoluidide (**3c**) was oxidized by 3 equiv of

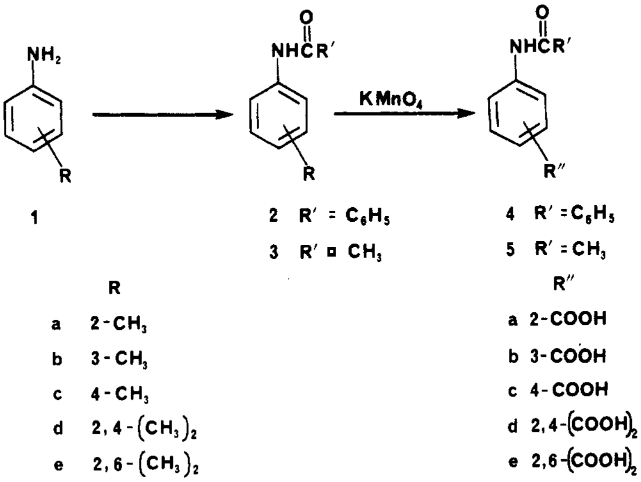

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Table II. Decomposition of $KMnO_4$ Catalyzed by Amides[a]

entry	amide	solubility[b]	recovery of amide,[c] %	change of $KMnO_4$,[c,d] %	MnO_2,[c,e] %
1	CH_3CONH_2	soluble	95	0	0
2	$C_6H_5CONH_2$	soluble	60	30	30
3	$CH_3CONHC_6H_5$	soluble	95	100	>95
4	$C_6H_5CONHC_6H_5$	soluble	95	100	>95
5	$C_6H_5CON(CH_3)_2$	partially soluble	15	95	>95
6	$CH_3CON(C_6H_5)_2$	partially soluble	80	67	80
7	$C_6H_5CON(C_6H_5)_2$.	insoluble	95	0	0

[a] Amide:$KMnO_4$ = 1:2 by mole; reflux for 3 h. [b] Determined separately by heating 12.5 mmol of amide in 250 mL of water to boil. [c] The yields are average values of at least three runs. [d] Monitored by UV absorption. [e] Calculated from initial amount of $KMnO_4$.

$KMnO_4$ in neutral aqueous solution to give the acid **5c** in 60–70% yield.[4] The ortho isomer **3a** was reported to give a 95% yield of the corresponding acid (**5a**) under alkaline conditions although the procedure seems ambiguous.[5] Hydrolysis was reported under the alkaline conditions.[6] Hydrolysis of the amide protecting group would complicate the whole reaction because the free amino group should be oxidized readily by $KMnO_4$.[7] Therefore, the reaction should be carried out in neutral solution. Xylidides **2e** and **3e** were oxidized to **4e** and **5e**, respectively;[8] $CaMnO_4$ was used for oxidation of **3d** to **5d**.[9]

Our results are shown in Table I. Except for *p*-acetotoluidide (**3c**), the oxidation reaction with both *N*-benzoyl (**2**) and *N*-acetyl (**3**) compounds gave low yields of the corresponding (*N*-acylamino)benzoic acids **4** and **5**. Benzotoluidides **2a–c** seemed to be more sluggish in oxidation than acetotoluidides **3a–c**. However, xylidides **2d**,**e** and **3d**,**e** are more resistive to oxidation than toluidides regardless of the nature of the protecting groups. This may be due to the low solubility of **2a–c** in water. Although the isolated yields of (*N*-acylamino)benzoic acids **4** and **5** were low and significant amounts of starting materials were recovered, MnO_2 was produced almost quantitatively in each case (Table I). It is known that MnO_2 catalyzes the decomposition of $KMnO_4$ to MnO_2.[10] We tried to find out to what extent the decomposition of $KMnO_4$ by MnO_2 took place under the reaction conditions, refluxing for 3 h in aqueous solution. Thus, mixtures of $KMnO_4$ (25.0 mmol) and varying amounts of MnO_2 (2.5, 5.0, 12.5, and 25.0 mmol) in H_2O (250 mL) were heated at reflux for 3 h, and the increase in the weight of MnO_2 was examined. But the increase was rather insignificant: 1–3%. Therefore, we ruled out the contribution of MnO_2 as a catalyst in the decomposition of $KMnO_4$ under the present conditions. Furthermore, self-decomposition of $KMnO_4$ under similar conditions was also shown to be insignificant by several blank runs. These observations led us to suspect that the decomposition of $KMnO_4$ might have been catalyzed by the substrates **2** and **3**.

Table III. Rate Constants of the Formation of Oxygen from the Reaction of Secondary Amides and $KMnO_4$[a]

amide	k_{obsd}, 10^2 s^{-1}	amide	k_{obsd}, 10^2 s^{-1}
3a	2.85	$CH_3CONHC_6H_5$	6.44
3b	1.35	$C_6H_5CONHC_6H_5$	3.81
3c	4.01		

[a] See Experimental Section.

Table IV. Reactions of *p*-Benzotoluidide (2c) with Various Oxidizing Agents

reagent	solvent	condtns	product (%)
$Na_2Cr_2O_7$	H_2O	reflux, 8 h	starting material (90)
60% HNO_3	–	reflux, 1 h	benzoic acid (95)
$HClO_4$	–	reflux, 2 h	benzoic acid (95)
SeO_2–H_2O_2	H_2O	reflux, 45 h	benzoic acid (80)
SeO_2	CH_3COOH	reflux, 26 h	starting material (95)
$Co(OCOCH_3)_2$ NaBr, O_2	CH_3COOH	100 °C, 3 h	starting material (95)

Substrates **2** and **3** are secondary amides that have oxidizable methyl groups. In order to examine the effect of amides on the decomposition of $KMnO_4$, a group of representative amides were heated with aqueous $KMnO_4$ for 3 h. The results are listed in Table II. Monosubstituted amides (entries 3 and 4) seemed to facilitate the decomposition of $KMnO_4$ much more effectively than unsubstituted ones (entries 1 and 2). Disubstituted amides showed different characteristics: no change of $KMnO_4$ with *N*,*N*-diphenylbenzamide (entry 7), whereas significant changes of $KMnO_4$ with *N*,*N*-dimethylbenzamide (95%, entry 5) or with *N*,*N*-diphenylacetamide (67%, entry 6). With acetanilide (entry 3) or benzanilide (entry 4), the change took place within an hour and MnO_2 was isolated almost quantitatively. A test for the presence of Mn(II) (adding NH_4OH and then bubbling H_2S) was negative. The disappearance of $KMnO_4$ was also monitored by visible spectroscopy although no attempt was made to deduce kinetic parameters. Instead, the percentage of the decrease in absorbance at 546 nm was measured to confirm the change of the oxidizing agent. As shown in Table II, acetamide (entry 1) and *N*,*N*-diphenylbenzamide (entry 7) did not cause any reaction of $KMnO_4$. On the other hand, benzamide (entry 2), *N*,*N*-dimethylbenzamide (entry 5), and *N*,*N*-diphenylacetamide (entry 6) caused decomposition of ca. 30%, 95%, and 67%, respectively, after 3 h of reflux.

The byproduct of the thermal decomposition of $KMnO_4$ is oxygen as shown in eq 2.[10] Oxygen was indeed evolved,

$$2MnO_4^- + H_2O \rightarrow 2MnO_2 + 2OH^- + \tfrac{3}{2}O_2 \qquad (2)$$

as confirmed by formation of smoke upon contact with yellow phosphorus. We measured the increase in volume of the evolved oxygen. This accurately fitted the form of a pseudo-first-order rate law, and we were able to calculate

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Table V. Spectral Data of (*N*-Acetylamino)benzoic Acids 4 and 5

	IR,[a] cm^{-1}				NMR,[b] δ			
compd	$\nu_{NH,OH}$	$\nu_{C=O}$	amide-II	ρ_{OH}	Ar H	NH[d]	COOH[e]	UV,[c] nm (log ε)
4a	3400–2500	1685, 1642	1535	900	7.18 (m, 1 H), 7.60 (m, 4 H), 8.00 (m, 3 H), 8.73 (d, 1 H, *J* = 8.0 Hz)	6.00	10.00	231 (4.30), 270 (4.06), 306 (3.92)
4b	3300, 3250–2500	1705, 1685, 1645	1540	935	7.50 (m, 5 H), 7.90 (m, 3 H), 8.35 (apparent t, 1 H)	11.80	10.40	228 (4.26), 263 (4.05)
4c	3330, 3250–2500	1680, 1650	1520	930	7.55 (m, 3 H), 7.85 (m, 6 H)	11.50	10.50	224 infl (4.09), 280 (4.38)
4d	3500–2500	1690, 1670	1528	925	7.65 (m, 3 H), 8.10 (m, 3 H), 8.75 (m, 2 H)	11.50	12.30	232 (4.33), 280 (4.23), 285 infl (4.22), 297
4e	3500–2500	1710, 1695, 1660	1515	942	7.40 (m, 4 H), 7.90 (m, 4 H)	10.50	11.50	230 (4.29), 276 (3.88)
5a	3300–2500	1695, 1650	1525	965	7.05 (apparent t, 1 H, H-3, *J* = 8 Hz), 7.50 (dt, 1 H, H-5, *J* = 8 and 2 Hz), 7.85 (dd, 1 H, H-4, *J* = 8 and 2 Hz), 8.35 (d, 1 H, H-6, *J* = 8 Hz), 2.12[f]	11.50	11.01	251 (4.16), 303 (3.66)
5b	3300, 3200–2500	1705	1560	980	7.00–7.85 (m, 3 H), 8.15 (d, 1 H, H-2, *J* = 1 Hz), 2.05[f]	11.90	10.15	221 (4.11), 237 infl (3.83), 292 (2.84)
5c	3300, 3200–2500	1670	1520	935	AB pattern centered at 7.66, 7.86 (4 H, *J* = 7.6 Hz), 2.07[f]	11.50	10.10	267 (4.66)
5d	3400–2500	1720, 1695, 1655	1525	970	8.25 (d, 1 H, H-5, *J* = 8 Hz), 8.50 (s, 1 H, H-2), 8.55 (d, 1 H, H-6, *J* = 8 Hz), 2.17[f]	11.50	10.50	265 (4.20), 273 (4.19), 310 (3.76)
5e	3550, 3450–2500	1720, 1700, 1675	1510	955	AB_2 pattern centered at 7.30, 7.91 (3 H), 2.02[f]	11.00	10.00	218 (4.10), 260 (3.70)

[a] KBr. [b] DMSO-d_6. [c] Ethanol. [d] Broad peak. [e] Singlet. [f] Singlet, 3 H, $COCH_3$.

the rate constants for formation of oxygen in the reactions of **3a–c** with $KMnO_4$. The results are listed in Table III. Although we cannot propose a mechanism for the decomposition of $KMnO_4$ catalyzed by the secondary amides **2** and **3** from the data, it is quite clear that the catalytic activity is involved.

A unique, and the best, procedure in the literature for the oxidation of acetotoluidides **3a,c** was to employ $Co(OCOCH_3)_2$ together with oxygen (1 atm) and CH_3COOH at 100 °C.[11] We repeated a similar procedure by blowing O_2 but recovered only starting material. We extended our investigation of the oxidation reaction to various reagents, and the results are listed in Table IV. It seemed to be difficult to oxidize the methyl group without affecting the blocking group.

Experimental Section

Melting points were determined on a Fisher Mel-Temp apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 1430 spectrophotometer, and ultraviolet-visible spectra were recorded on a Hitachi U-3200 double-beam spectrophotometer. NMR spectra were recorded on a Varian EM-360L 60-MHz spectrometer.

Starting Materials. Benzotoluidides **2a–c** and xylidides **2d,e** and their aceto analogues **3a–e** were prepared by methods from the literature.[12-15] Carboxylic acid derivatives were identified by comparing melting points with the literature and by examining their spectra (Table V). Commercial amides were used for the experiments listed in Table II. $KMnO_4$ (reagent grade) was purchased from Junsei Chemical Co., Tokyo, Japan. Deionized water was distilled by means of a Corning Mega-Pure Water Still apparatus.

Oxidation Reactions of 2 and 3. A Representative Procedure. A mixture of **2** or **3** (6.7 mmol) and H_2O (50 mL) was heated (60–90 °C) to maximize dissolution. Homogeneous solutions resulted from **3a–c**, but other amides (**2a–e**, **3d,e**) were not completely dissolved. A solution of $KMnO_4$ (26.8 mmol, 4 equiv) in H_2O (150 mL) was added slowly (ca. 15 min). The mixture was heated at reflux for 1.5 h and cooled to room temperature. The solid was collected by filtration and washed with water several times. After the water was removed by suction as much as possible, the solid was suspended in absolute ethanol (100 mL) and filtered. The residue was dried under vacuum to give MnO_2. The ethanol filtrate was evaporated to dryness to give unreacted starting material, which was combined with the material from the ethereal extract of the aqueous filtrate (see below).

The aqueous filtrate was extracted with ether (3 × 50 mL), and the ethereal solution was dried with Na_2SO_4. After evaporation, unreacted starting material was obtained, which was combined with the solid from the ethanol extract above and dried under vacuum (0.1 mmHg) at 50 °C. The identity of the recovered amide was established by comparing its melting point and IR spectrum with those of an authentic sample. The aqueous solution was then acidified with concentrated HCl to pH 2–3, the temperature being kept below 5 °C. The precipitate was collected by filtration, washed with cold water, and dried under vacuum to give (*N*-acetylamino)benzoic acids **4** and **5**.

Oxidation of Amides with $KMnO_4$. A mixture of amide (12.5 mmol) and $KMnO_4$ (25.0 mmol) in H_2O (250 mL) was heated at reflux for 3 h.[16] After cooling to room temperature, the mixture was filtered and the residue was washed with an excess of water. The residue (MnO_2 and starting material) was suspended in absolute ethanol (100 mL) and filtered to give a solid mass of MnO_2. The ethanol filtrate was concentrated to give starting material, and its structure was confirmed by comparing its melting point and IR spectrum with those of an authentic sample. The aqueous filtrate was extracted with ether (3 × 75 mL) to ensure the complete recovery of unreacted starting materal.

Measurement of Rate of Evolution of Oxygen. At first, the void volume of a reaction assembly (500-mL round-bottomed

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flask equipped with a condenser whose top was connected by a Tygon tube to a 1000-mL graduated cylinder filled with water) was determined by heating a solution of $KMnO_4$ (25.3 mmol) in H_2O (250 mL) at reflux. The amides employed in the experiment are completely soluble in H_2O at the boiling temperature. A mixture of an amide (6.3 mmol) and $KMnO_4$ (25.3 mmol) was heated at boiling, and the volume of the evolved gas was measured at the predetermined time intervals. The evolution of the gas stopped after ca. 1 h from the beginning of boiling, and the volume of the gas reached to ca. 80% of the theoretical value. The rate constant was calculated graphically from the slope of a plot of time vs log $(V_t - V_0)$, where V_0 is the void volume.

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Uranium Metallacycle $[(Me_3Si)_2N]_2\overline{UCH_2SiMe_2N}SiMe_3$: A Mild Reagent for the Synthesis of Methyl Ketones from Nitriles

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The reaction of nitriles with Grignard reagents is a widely applicable synthetic route to ketimines, which by facile hydrolysis give ketones. However, this reaction suffers some limitations. With aliphatic nitriles, a serious complication arises due to the acidity of the α-hydrogen atom. If strongly basic solvents are used, they compete with the nitrile in formation of an organomagnesium complex. If organolithium reagents are used instead of Grignard reagents, the greater basicity of both lithium reagent and the product ketimine salt causes even more difficulty.

There is one report concerning the reaction of organotitanium reagents with benzonitrile to produce acetophenone;[1] however, it seems that the reaction of hydrocarbyl–metal compounds with nitriles has been little investigated.

In a previous paper, we described the specific reaction of tris(hexamethyldisilylamino)methyluranium with aliphatic nitriles to give azomethine complexes.[2] After hydrolysis, methyl ketones were isolated in high yield. Andersen et al. have also shown that *tert*-butyl cyanide inserted readily in the uranium–methylene bond of the metallacycle $[(Me_3Si)_2N]_3\overline{UCH_2SiMe_2N}SiMe_3$ (1), affording the expected six-membered metallacycle in which the reduced *tert*-butyl cyanide group was structurally related to an azomethine.[3]

We report here a specific, rapid, clean, and high-yield reaction of nitriles to give the corresponding methyl ketones by using the uranium metallacycle 1 in nonbasic solvents.

Scheme I

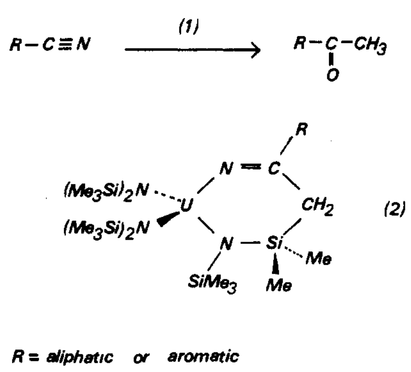

Table I. Representative Reactions of Nitriles RC≡N with $[(Me_3Si)_2N]_2\overline{UCH_2SiMe_2N}SiMe_3$ To Give the Methyl Ketones $RC(O)CH_3$

entry	substrate R(RC≡N)	metallacycle 2 yield,[a] %	product RC(O)CH$_3$ yield,[b] %
A	CH_3	88	42
B	$CH_3CH_2CH_2$	86	47
C	$(CH_3)_2CH$	86	48
D	$C_6H_5CH_2$	85	66
E	$(C_6H_5)_2CH$	83	70
F	CH_2═CH	78	68
G	$BrCH_2CH_2$	80	70
H	C_6H_5	84	68
I	o-ClC_6H_4	75	72
J	N≡CCH_2CH_2	73	–

[a] On isolated compound. [b] By VPC after hydrolysis.

The stoichiometric reaction of 1 with aliphatic or aromatic nitriles was performed at room temperature (Scheme I). Pure and diluted nitriles were added dropwise to a stirred solution of 1 in pentane or toluene. After hydrolysis with dilute HCl, only the methylketones were obtained in the organic layer.[4] They can be isolated in high yield by TLC or VPC. Results obtained with some representative nitriles are summarized in Table I.

Uranium metallacycle 1 reacts with a variety of nitriles to produce metallacycles 2, which are isolated in 73–88% yields.[5] Methyl ketones are produced in 42–72% yield after hydrolysis. Entries A–E and H illustrate the very important point that the metallacycle 1 reacts exclusively with the C≡N group of aliphatic or aromatic nitriles, even in the case of acetonitrile and diphenylacetonitrile, which give very poor yields of ketone with Grignard reagents. The reaction gives also high yields with acrylonitrile (entry F). Entries G and I establish that the reaction can be extended to halogenated nitriles without a concurrent uranium–halogen substitution reaction. Unfortunately, it was impossible to isolate well-defined products from dinitriles (entry J). However a NMR-monitored reaction showed the quantitative formation of the monoinserted compound. The second cyano group was unreactive, even when an excess of metallacycle 1 was added.

The structures of metallacycles 2 were easily established by IR and NMR spectroscopy. The IR spectra showed an intense peak at ca. 1620 cm^{-1} attributable to the C═N

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(4) In fact, $HN(SiMe_3)_2$ and probably an aminosilanol were formed after hydrolysis of 2. These amino compounds form ammonium salts with HCl and are dissolved in the aqueous layer.

(5) ^1H NMR monitored reactions (in C_6D_6) show the complete consumption of 1 and the quantitative insertion of the nitriles to give 2; no additional peaks that could be attributed to the 54 $N(SiMe_3)_2$ protons of the reaction products between the nitrile anion and 1: $[(SiMe_3)_2N]_3UCH(R)C$≡N were detected.

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