Restricted Rotation in Amides. 8. Steric and Electronic Effects on Lanthanide–Amide Equilibria[1]

Anita H. Lewin* and R. Alekel[2]

Contribution from the Department of Chemistry, Polytechnic Institute of New York, Brooklyn, New York, 11201. *Received July 28, 1975*

Abstract: The binding strengths of tertiary amides to $Eu(DPM)_3$ (relative to the binding strength of DMF) were determined for a series of formamides, acetamides, and benzamides. It was found that the equilibrium constant for the amide–europium complex is subject to a combination of steric and electronic effects and depends on the configuration of the amide. Thus, resonance assignments, using lanthanide induced shifts may be unreliable in unsymmetrically N-substituted tertiary amides.

Lanthanide induced shifts have found varied and extensive applications over the last few years.[3] It is generally accepted that the magnitude of the lanthanide induced shift (LIS) is dominated by the pseudocontact shift, which is related to the distance between the proton under observation and the lanthanide ion, the angle which this vector makes with the principal magnetic axis of the molecule, and the equilibrium constant for complexation of the substrate with the lanthanide complex.[3] Determination of the absolute values of equilibrium constants for a few substrates has been reported[3-6] and relative binding strengths of various functional groups have been determined, using competition experiments.[6,7] It is known that, in general, the sequence for binding strength is:[8] alcohol > ketone > ether > ester. Substantial variations in binding strength, due to relatively minor structrual changes, have been reported[3] but no systematic study of electronic and steric effects on the lanthanide-substrate equilibrium is available.

Amides have been found to complex with europium[3,8,9] and it has been shown,[9] using amides for which resonance assignments had been made previously by other methods, that a group suffers a considerably larger LIS when it is syn to the carbonyl oxygen than when it is anti to it. In the absence of other σ donating groups LIS's apparently provide a rapid and convenient method for making resonance assignments in symmetrically N-substituted tertiary amides for which resonances for both amide isomers are seen. Configurational assignments for amides exhibiting the presence of only one isomer based on similarity in LIS values for related systems have been found to lead to correct conclusions.[10] However, such assignments are tenuous since neither the geometry nor the equilibrium constants of the amide–lanthanide complexes are known and, therefore, LIS values should not be compared. The LIS method has also been used for assigning the resonances in unsymmetrically N-substituted tertiary amides, but it has been pointed out that it might lead to erroneous results if one of the amide isomers would complex preferentially with the lanthanide shift reagent.[10] As part of our continuing investigations of amides, we have undertaken to study the steric and electronic effects on equilibrium constants of lanthanide–amide complexes.

Results

The shifts induced in the methyl group syn to the carbonyl oxygen of dimethylformamide (DMF) in CCl_4 with varying amounts of added europium(III) tris(2,2,6,6-tetramethyl-3,5-heptadione) [$Eu(DPM)_3$] were determined and gave a good least-squares fit with a slope of 599 Hz and an intercept of 0.5 Hz. The induced shifts for the same methyl group in DMF were then recorded for equimolar solutions of DMF (0.1 M) and another amide (0.1 M) in the presence of 0.02 M $Eu(DPM)_3$. The effect of varying the N-substituents and the variations in acetamides and *p*-chlorobenzamides vis-a-vis DMF as well as the effects of benzoyl substituents in *N,N*-dibenzylbenzamides are listed in Table I.

Discussion

The observed LIS for any substrate is a function of the geometry of the lanthanide–substrate complex and of the lanthanide–substrate equilibrium. Since both of these would most likely vary as structural and electronic changes are introduced in the substrate, evaluation of the equilibrium constant is not straightforward. At the same time, the relative magnitudes of a series of equilibrium constants (K) are sufficient in order to

Table I. Lanthanide Induced Shifts in the Syn Methyl Group of Dimethylformamide (X) in the Presence of Other Amides (Y)[a]

Amide (Y)	Observed shift (Hz)[b]	Differential shift (Hz)[c,d]
Formamides: N-Substituents		
Dimethyl	228.5	–
Dibenzyl	239.5	11.0
Diethyl	216.0	−12.5
Diisopropyl	201.0	−27.5
N-Benzyl-*N*-methyl	230.5	2.0
N-Benzyl-*N*-isopropyl	226.0	−2.5
N-Benzyl-*N*-*tert*-butyl	214.0	−14.5
Acetamides: N-Substituents		
Dimethyl	201.0	−27.5
N-Benzyl-*N*-methyl	211.0	−17.5
N-Benzyl-*N*-ethyl	209.0	−19.5
N-Benzyl-*N*-isopropyl	210.5	−18.0
N-Benzyl-*N*-*tert*-butyl	216.0	−12.5
N-Alkyl-*N*-benzyl-*p*-chlorobenzamides: *N*-Alkyl		
Methyl	254.0	25.5
Isopropyl	249.5	21.0
tert-Butyl	269.0	40.5
N,N-Dibenzylbenzamides: Benzoyl Substituent(s)		
H	267.0	38.5
2-CH_3	278.0	49.5
3-CH_3	267.0	38.5
4-CH_3	267.5	39.0
2-Cl	283.0	54.5
3-Cl	275.0	46.5
4-Cl	270.0	41.5
2,4-Cl_2	286.0	57.5
4-F	272.0	43.5

[a] 0.1 M X + 0.1 M Y + 0.02 M $Eu(DPM)_3$ in CCl_4; 60 MHz; 37 °C. [b] Observed shift of the syn methyl group in X in the presence of Y. [c] Shift in the presence of Y—shift in the absence of Y. [d] Positive numbers indicate a downfield shift.

Table II. Binding Constants of Amides to $Eu(DPM)_3$[a]

No.	Amide	Binding constant Relative to DMF	Binding constant Relative to X	% B[b]
	Formamides: N-Substituents			
1	Dimethyl	1.00		–
2	Dibenzyl	0.66		–
3	Diethyl	1.59		–
4	Diisopropyl	2.97		–
5	*N*-Benzyl-*N*-methyl	0.92		46[c]
6	*N*-Benzyl-*N*-isopropyl	1.09		65[c]
7	*N*-Benzyl-*N*-*tert*-butyl	1.72		89[c]
	Acetamides: N-Substituents		X = DMA[d]	
8	Dimethyl	2.97	1.00	–
9	*N*-Benzyl-*N*-methyl	1.94	0.65	69[c]
10	*N*-Benzyl-*N*-ethyl	2.10	0.71	55[c]
11	*N*-Benzyl-*N*-isopropyl	1.98	0.67	37[c]
12	*N*-Benzyl-*N*-*tert*-butyl	1.59	0.54	0[c]
	N-Alkyl-*N*-benzyl-*p*-chlorobenzamides: N-Alkyl		X = DBPCB[e]	
13	Benzyl	0.154	1.00	–
14	Methyl	0.364	2.36	60[f]
15	Isopropyl	0.442	2.87	30[f]
16	*tert*-Butyl	0.164	1.06	0[f]
	N,*N*-Dibenzylbenzamides: Benzoyl substituents		X = DBB[g]	
17	H	0.186	1.000	–
18	2-CH_3	0.077	0.414	–
19	3-CH_3	0.186	1.000	–
20	4-CH_3	0.181	0.973	–
21	2-Cl	0.037	0.198	–
22	3-Cl	0.104	0.559	–
23	4-Cl	0.154	0.827	–
24	2,4-Cl_2	0.0151	0.081	–
25	4-F	0.133	0.715	–

[a] In CCl_4 at 37 °C. [b] Isomer with benzyl group syn to carbonyl oxygen. [c] From ref 10. [d] DMA = dimethylacetamide. [e] DBPCB = dibenzyl-*p*-chlorobenzamide. [f] From ref 13. [g] DBB = dibenzylbenzamide.

investigate steric and electronic effects on K. We have, therefore, determined K for various amides with $Eu(DPM)_3$, relative to K for dimethylformamide (DMF). In order to sidestep problems arising from changes in the amide-$Eu(DPM)_3$ complex with different amides, we have used the LIS of DMF in the presence of an equimolar concentration of another amide and of a limiting concentration of $Eu(DPM)_3$. Since neither the structure nor the equilibrium constant of the DMF-$Eu(DPM)_3$ complex is likely to be affected by the presence of another amide, the LIS of DMF (δ) should accurately represent the concentration of the complex. In our experiments the initial concentration of DMF was 0.1 M, therefore at equilibrium

$$[C_X] = 0.1(\delta - \delta_X)/(\delta_X^{Eu} - \delta) \quad (1)$$

where X and C_X represent DMF and its $Eu(DPM)_3$ complex, δ_X is the chemical shift of DMF in the absence of $Eu(DPM)_3$ and δ_X^{Eu} is the chemical shift of the $Eu(DPM)_3$ complex of DMF. Evaluating $(\delta_X^{Eu} - \delta)$ by extrapolation of the plot of $\Delta\delta$ vs. ρ and using eq 1, $[C_X]$ was calculated from the LIS values in Table I.

The concentration of any amide-$Eu(DPM)_3$ complex[15] is a function of the concentrations of the amide and of $Eu(DPM)_3$ and of the formation constant. Using DMF, X, and another amide, Y, with initial concentrations 0.1 M and adding $Eu(DPM)_3$ with initial concentration 0.02 M the ratio K_Y/K_X can be expressed as

$$\frac{k_Y}{K_X} = \frac{[C_X]^2 - 0.12[C_X] + 0.002}{[C_X]^2 + 0.08[C_X]} \quad (2)$$

assuming that K_X and K_Y are both very large. The only unknown in eq 2 is $[C_X]$ which was evaluated using eq 1. Using these calculated values and eq 2 K_Y/K_X values for several amide series were calculated (Table II).

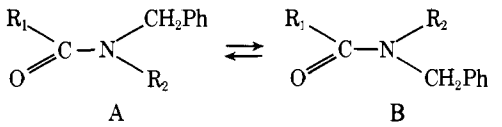
Examination of Table II reveals a factor of four on the amide-$Eu(DPM)_3$ binding constant K_{Eu}, resulting from replacement of the *N*-methyl groups of dimethylformamide by other alkyl substituents (entries 1–4). Complexation of amides with lanthanides has been shown to be through oxygen[3,8,9] and the observed effect of the N-substituents on the binding constants is consistent with the donor properties of the carbonyl oxygen in these substituted formamides. Thus, substituents which are electron donors (isopropyl, *tert*-butyl) enhance the donor properties of the carbonyl oxygen by increasing the electron density in the amide linkage (entries 3 and 4). Conversely, electron withdrawal, as by benzyl groups, decreases the electron density in the amide and consequently leads to lower binding constants (entry 2). Parallel behavior has been observed for amide basicity.[11]

Replacing the formyl hydrogen has an analogous effect. Dimethylacetamide binds $Eu(DPM)_3$ three times as effectively as dimethylformamide, due to electron donation by the acetyl methyl (entries 1 and 8) and dibenzylbenzamide binds $Eu(DPM)_3$ three times less effectively than dibenzylformamide (entries 2 and 17) because of electron withdrawal by the benzoyl phenyl. The extension of this effect is seen in the series of benzoyl substituted *N*,*N*-dibenzylbenzamides, where it may be noted that, as expected, introduction of a methyl group onto the benzoyl phenyl in either the 3 or 4 position exerts essentially no effect on K_{Eu} (entries 17, 19, 20). At the same time introduction of chloro and fluoro groups has the expected effect on K_{Eu}. Namely, a 3-chloro substituent (entry 22) decreases K_{Eu} substantially due to inductive electron withdrawal by chlorine; 4-substitution (entries 23 and 25) has a smaller effect because of resonance donation, which is greater for fluorine than for chlorine.

The binding constants for ortho-substituted benzamides are seen to be very much lower than any of the others. Whereas for 2-chloro (entry 21) it could be argued that this is a consequence of the inductive effect; the magnitude of the decrease in binding constant when the values for the 2- and 4-chloroamides (entries 21 and 23) are compared seems too large (4.2). Furthermore, the effect of the 2-methyl group (entry 18) is entirely inconsistent with an explanation based on inductive effects. It has been shown that in ortho-substituted benzamides the benzoyl phenyl is twisted out of the plane of the amide linkage.[10,12] This effectively removes resonance contribution to the carbonyl entirely and leaves only the inductive electron withdrawing effect of the benzoyl phenyl, thus making the carbonyl a poor donor indeed. The combination of these steric and electronic effects leads to quite substantial changes in K_{Eu} as can be seen in the case of *N*,*N*-dibenzyl-2,4-dichlorobenzamide (entry 24) where K_{Eu} is only 8% of that for the unsubstituted amide.

The unsymmetrically N-substituted formamides (Table II, entries 5–7) exhibit a trend in K_{Eu} values consistent with the general effect of N-substitution although the effect of an isopropyl group seems to be too small as compared to the effect of a methyl group. The correlation breaks down completely, however, in the unsymmetrically N-substituted acetamides (entries 9–12), and *p*-chlorobenzamides (entries 14–16). For example, although inductive donation by a *tert*-butyl group should enhance the value of K_{Eu} as is the case for *N*-benzyl-*N*-*tert*-butylformamide, it, in fact, decreases the value of K_{Eu} in both the acetamide and the *p*-chlorobenzamide. This apparent contradiction can be resolved by considering the isomer

composition of the unsymmetrically N-substituted amides[10,13] (Table II). Thus the trend in the magnitude of K_{Eu} roughly



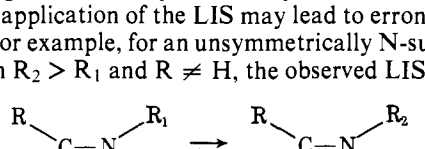
A B

follows the isomer composition; as the percentage of isomer B in the mixture increases, so does K_{Eu}.

In the *N*-alkyl-*N*-benzylformamides the percentage of isomer B increases in parallel with the electron donor ability of the N-substituents, in accord with the generalization that the major isomer in formamides has the bulky group on the more "spacious" side of the amide linkage, i.e., syn to the small formyl hydrogen and anti to the carbonyl oxygen.[14] Since for the alkyl groups investigated the inductive electron donating ability increases with the bulk of the alkyl group, the isomer composition of the amide and the electronic effect of the alkyl group operate in the same direction, namely, to increase K_{Eu}. The opposite situation holds in all other amides. Thus, the major isomer in *N*-alkyl-*N*-benzylacetamides is expected to have a configuration opposite that of the analogous formamides, since the "spacious" side of the amide linkage is now syn to the carbonyl oxygen.[14] In fact, it has been found that for acetamides, the bulky group is syn to the carbonyl oxygen in the major isomer[9] and consequently the values of K_{Eu} represent a combination of effects. As the bulk of the *N*-alkyl group increases, so does its inductive electron donation and therefore K_{Eu} should increase as well. At the same time, as the bulk of the alkyl group increases, the percentage of isomer B in the mixture decreases, leading to a decrease in K_{Eu}. Essentially the same effect is seen in *N*-alkyl-*N*-benzyl-*p*-chlorobenzamides. The *N*-*tert*-butylamide which exists entirely in configuration A is much weaker in binding $Eu(DPM)_3$ than the analogous *N*-methylamide, in which the major isomer (60%) has configuration B.[13]

Since the magnitude of K_{Eu} in unsymmetrically N-substituted tertiary amides depends on the isomer composition, it follows that the binding constants for the two amide isomers, A and B, must be different. In fact, the data strongly suggest that the binding constant for isomer B exceeds that for isomer A in most cases. Intuitively this is not unlikely. A striking case of steric effects on the lanthanide-ketone binding constant has been reported.[6] For amides, it seems entirely reasonable to expect that in isomer A, which has the bulky group syn to the carbonyl oxygen, there could be steric hindrance to complexation of the lanthanide, relative to isomer B.

The order of group size in amides has been shown to be[10] H $<$ O $<$ CH_3 $<$ CH_2CH_3 $<$ CH_2Ph $<$ $CH(CH_3)_2$ $<$ $C(CH_3)_3$. It might be expected that in unsymmetrically N-substituted amides the isomer with the larger K_{Eu} would be that with the smaller group syn to the carbonyl oxygen, namely, the minor isomer (except in formamides). If this indeed is the case, resonance assignments in unsymmetrically N-substituted tertiary amides by application of the LIS may lead to erroneous conclusions. For example, for an unsymmetrically N-substituted amide with $R_2 > R_1$ and $R \neq H$, the observed LIS for R_2 in



A B

A should exceed that in B and vice versa for R_1, provided that the lanthanide binding constants are the same for A and B. However, since it appears that the presence of a bulky group syn to the carbonyl oxygen serves to decrease the lanthanide-amide binding constant, it follows that for the system under consideration K_B would be larger than K_A. Thus, if the two isomers were equally populated in the uncomplexed amide, the concentration of the lanthanide-amide complex of isomer B, $[C_B]$, would exceed that of the complex of isomer A, $[C_A]$. Since the observed LIS is a function of the complex concentration (eq 1) and $[C_B] > [C_A]$, it would be possible for the LIS of R_2 in B to be larger than the analogous shift in A, in spite of the fact that R_2 is closer to the site of complexation (i.e., the carbonyl oxygen) in A than in B. On the other hand, the LIS for R_1 in B would be larger than in A, as expected based solely on distance considerations. Finally, since A and B are unlikely to be equally populated when R_2 is larger than R_1 and, in fact, the concentration of A most likely exceeds that of B, no firm conclusions regarding the relative concentrations of the amide-lanthanide complexes C_A and C_B can be drawn for this hypothetical case. It is obvious, however, that for unsymmetrically N-substituted tertiary amides, use of the LIS method for resonance assignments needs to be approached with reservations. Further investigations to elucidate the situation are being undertaken.

Experimental Section

Amides. The amides used in this study were either commercially available or previously prepared.[1,10,13] Liquid amides were stored over Linde 3A molecular sieves.

Carbon Tetrachloride. Dried with and stored over Linde 3A molecular sieves.

Europium(III)-2,2,6,6-Tetamethyl-3,5-heptadione, [Eu(DPM)$_3$]. The shift reagent (Norell Chemical Co.) was sublimed at 165 °C (0.01 mmHg) and stored in a desiccator over P_2O_5 and under N_2.

Competition Experiments. The NMR spectrum of a 0.2 M CCl_4 solution of the amide to be used was recorded. A 0.5-ml sample of the solution was then pipetted into a 1-dram screw cap vial fitted with a Teflon cap liner. A 0.5-ml sample of the stock 0.2 M DMF solution was also pipetted in. The shift reagent, 14.02 mg, was weighed out into a dry Coors porcelain weighing boat which was inserted directly into the sample vial. Sufficient time was allowed for the dissolution of the shift reagent. All samples were inspected for turbidity and/or precipitation after addition of $Eu(DPM)_3$; none was found, all formed clear solutions.

NMR Spectra. All spectra were determined at 60 MHz, at a temperature of 37 °C, on a Varian A60-A spectrometer equipped with a ruggedized six-turn insert. The sample tubes were dried under vacuum at room temperature. In order to avoid involvement of Me_4Si in the competition for $Eu(DPM)_3$, chemical shifts were determined with respect to a solution of Me_4Si in CCl_4 which was placed in a coaxial inner tube.

References and Notes

(1) Part 7. A. H. Lewin and M. Frucht, *Org. Magn. Reson.*, 7, 206 (1975).
(2) (a) Taken in part from the Thesis of R. Alekel, submitted to the Faculty of the Polytechnic Institute of New York in partial fulfillment of the requirements for the degree of Master of Science in Chemistry, 1975. (b) Permission to use the laboratory facilities and tuition support afforded by the Schering Corporation are gratefully acknowledged.
(3) R. E. Sievers, Ed., "NMR Shift Reagents", Academic Press, New York, N.Y., 1973.
(4) I. Armitage, G. Dunsmore, L. D. Hall, and A. G. Marshall, *Chem. Commun.*, 1281 (1971); *Can. J. Chem.*, **50**, 2119 (1972); D. R. Kelsey, *J. Am. Chem. Soc.*, **94**, 1764 (1972); J. Bouquant and J. Chuche, *Tetrahedron Lett.*, 2337 (1972); R. K. Mackie and T. M. Shepherd, *Org. Magn. Reson.*, **4**, 557 (1972).
(5) B. L. Shapiro and D. Johnston, Jr., *J. Am. Chem. Soc.*, **94**, 8185 (1972).
(6) J. K. M. Saunders, S. W. Hanson, and D. H. Williams, *J. Am. Chem. Soc.*, **94**, 5325 (1972).
(7) J. K. M. Saunders and D. H. Williams, *J. Chem. Soc., Chem. Commun.*, 436 (1972); H. Hart and G. M. Love, *Tetrahedron Lett.*, 625 (1971).
(8) J. K. M. Saunders and D. H. Williams, *J. Am. Chem. Soc.*, **93**, 641 (1971).
(9) A. H. Lewin, *Tetrahedron Lett.*, 3583 (1971); L. R. Isbrandt and M. T. Rogers, *Chem. Commun.*, 1378 (1971).
(10) A. H. Lewin, M. Frucht, K. V. J. Chen, E. Benedetti, and B. DiBlasio, *Tetrahedron*, **31**, 207 (1975).
(11) R. B. Homer and C. C. Johnson, "The Chemistry of Amides", J. Labicky, Ed., Interscience, New York, N.Y., 1970, Chapter 3, and references therein; E. M. Arnett, *Prog. Phys. Org. Chem.* 1 (1963), and references therein.

(12) A. H. Lewin and M. Frucht, *Tetrahedron Lett.*, 1079 (1970); L. M. Jackman, T. E. Kavanaugh, and R. C. Haddon, *Org. Magn. Reson.*, 1, 109 (1969).
(13) A. H. Lewin and V. Mancini, unpublished work.
(14) L. A. LaPlanche and M. T. Rogers, *J. Am. Chem. Soc.*, **85**, 3728 (1963).
(15) Although a 2:1 amide-Eu(DPM)$_3$ complex has been isolated from saturated solutions of Eu(DPM)$_3$ in DMF[3] and two-step equilibria involving Eu(fod)$_3$ have been shown to be of importance in solution[5], no evidence for such stoichiometry for Eu(DPM)$_3$ in solution has been presented.[3,6] It is therefore assumed that a 1:1 stoichiometry obtains under our experimental conditions.

Synthesis and Structure of Dilithium Octamethyldirhenate(III)

F. Albert Cotton,* [1a] Larry D. Gage,[1a] Kostas Mertis,[1b] Larry W. Shive,[1a] and Geoffrey Wilkinson* [1b]

Contribution from the Departments of Chemistry, Texas A&M University, College Station, Texas 77843 and Imperial College of Science and Technology, London, United Kingdom. *Received April 5, 1976*

Abstract: The interaction of rhenium pentachloride or the carboxylato bridged compound $Re_2(O_2CC_6H_5)_4Cl_2$ with methyllithium in diethyl ether produces $Li_2Re_2(CH_3)_8 \cdot 2(C_2H_5)_2O$, a red crystalline air- and water-sensitive, but thermally stable, complex. The compound is diamagnetic and has a single sharp proton NMR line. Addition of *N,N,N′,N′*-tetramethylethylenediamine (tmed) or 1,10-phenanthroline (phen) yields the compounds $Li_2Re_2(CH_3)_8 \cdot$(tmed) and $Li_2Re_2(CH_3)_8 \cdot$(phen), respectively. The structure of the diethyl etherate has been determined by x-ray crystallography. Single crystals were formed from pentane and the following triclinic cell dimensions were obtained: a = 8.343 (4), b = 10.436 (3), c = 7.551 (2) Å, α = 106.91 (2)°, β = 96.59 (3)°, γ = 69.47 (3)°, and V = 589.0 (4) Å^3. The space group is $P\bar{1}$ with Z = 1 and the $Re_2(CH_3)_8^{2-}$ anion is situated on a crystallographic center of inversion. The anion is very similar in structure to those in the compounds $Li_4M_2(CH_3)_8 \cdot 4C_4H_{10}O$ (M = Cr or Mo). Bond distances and angles of greatest interest are: Re(1)–Re(1)′, 2.178 (1); average Re–C, 2.19 (1); Li–O, 1.94 (2) Å; average Re(1)–Re(1)′–C angle, 105.7 (4)°. The short metal–metal bond and eclipsed configuration in this complex are consistent with the presence of a Re–Re quadruple bond. The Re–Re distance here is equal, within the esd's, to the shortest such distance previously reported. The effect of van der Waal's forces on the rotational configuration of $Re_2X_8^{2-}$ species is discussed in greater detail than has heretofore been possible.

In recent years the existence and, indeed, wide occurrence of strong, short multiple metal-to-metal bonds has been recognized and verified.[2,3] The thermally stable tetralithium salts of octamethyldichromate(II), $Cr_2(Me_8)^{4-}$, and octamethyldimolybdenate(II), $Mo_2(Me)_8^{4-}$, are known and their structures have been determined.[4,5]

The corresponding isoelectronic octamethyldirhenate(III) anion, $Re_2(Me)_8^{2-}$, has not previously been isolated despite the large number of known complexes derived from ligand substitution reactions carried out on the $Re_2Cl_8^{2-}$ ion, where chloride can be replaced by other monodentate ligands with retention of the Re–Re quadruple bond.[3] Only one alkylrhenate ion has been previously described, namely the paramagnetic octamethylrhenate(VI)[6,7] in $Li_2[ReMe_8]$, obtained by action of methyllithium on hexamethylrhenium(VI). We have now found that the $Re_2Me_8^{2-}$ ion can be obtained either by action of MeLi on rhenium pentachloride in diethyl ether or by action of MeLi on the tetracarboxylato complex, $Re_2(OCC_6H_5)_4Cl_2$, which already has a rhenium–rhenium quadruple bond.

Experimental Section

Microanalyses were performed by Imperial College and Butterworth Analytical Laboratories. Direct analysis of methyl groups was accomplished by hydrolysis of the complexes with deoxygenated water; the methane evolved was measured by a gas buret. The rhenium in the residual solution was determined by plasma arc atomic absorption spectroscopy. NMR spectra were recorded on Perkin-Elmer R14 (60 MHz) and Varian HA 100 spectrometers.

Syntheses. All syntheses and manipulations were carried out in oxygen-free nitrogen or argon. Solvents or reagents were freshly prepared, purified, dried, and degassed. Glass apparatus was dried by heating under vacuum before use. The rhenium used was reagent quality powder (99.9% BDH). Solutions of the products are extremely sensitive to air and moisture and the solid dietherate is pyrophoric. Rhenium pentachloride was freed from the volatile impurity $ReOCl_4$ by pumping under vacuum for several hours. Methyllithium was prepared in diethyl ether from lithium and methyl chloride or purchased from Ventron Corp., Beverly, Mass. $Re_2(O_2CC_6H_5)_4Cl_2$ was prepared as previously reported.[8]

Dilithium Octamethyldirhenate(III) Bis(diethyl ether). A. From Rhenium Pentachloride. To a solution of $ReCl_5$ (3.6 g, 0.01 mol) in diethyl ether (70 cm^3) was added at −78 °C, slowly and under rapid stirring, a solution of MeLi 0.9 M in ether (100 cm^3, 0.09 mol). The solution was prepared by cooling the $ReCl_5$ at −78 °C and by adding 70 cm^3 of melting diethyl ether previously frozen in liquid nitrogen. The reaction mixture was left to warm up slowly. The solution became red at −38 °C and bright red crystals precipitated. After warming to room temperature, the solution was filtered quickly, the filtrate reduced to a small volume (60 cm^3), and the product crystallized in the form of bright-red crystals by cooling at −78 °C. These were filtered at −78 °C, washed with successive 25-cm^3 portions of diethyl ether at −78 °C, and dried at −20 °C (10^{-3} mmHg) to give 2.2 g of the compound, yield 16%, based on $ReCl_5$: Re:Li determination, calcd 1.00; found 1.02; CH_4 determination, calcd Re:CH_4 1:4; found 1:4.17; ^{1}H NMR (benzene) τ 9.21 (s, Re–CH_3), 6.58 (q, –OCH_2CH$_3$), 8.88 (t, –OCH$_2$$CH_3$).

B. From $Re_2(O_2CC_6H_5)_4Cl_2$. $Re_2(O_2CC_6H_5)_4Cl_2$ (0.5 g) and diethyl ether (30 ml) were placed in a round-bottom flask equipped with nitrogen inlets and immersed in liquid nitrogen, and $LiCH_3$ (20 cm^3 of a 1.7 M solution) was then introduced by means of a syringe. The reaction mixture was then allowed to warm to room temperature and stirred for an additional 2 h. The ether was removed by vacuum and four 20-cm^3 portions of pentane were used to extract the red $Li_2Re_2(CH_3)_8 \cdot 2Et_2O$ from the remaining solid. The resultant red solution was filtered through a fritted Schlenck tube, concentrated, and placed in a refrigerator at −40 °C in order to obtain a crystalline product.

The *N,N,N′,N′*-Tetramethylethylenediamine Salt, $Li_2[Re_2Me_8]$(tmed). Into a red ethereal solution (35 cm^3) of $Li_2[Re_2(Me)_8] \cdot 2Et_2O$ (0.5 g) of 0 °C was added slowly an ethereal solution of *N,N,N′,N′*-tetramethylethylenediamine (tmed). A light blue-purple crystalline solid precipitated immediately. This was collected by filtration at −78 °C, washed with several 20-cm^3 portions of diethyl ether at