Synthesis of Alkyl[hydrotris(pyrazolyl)borato]ruthenium(II) Complexes by Transmetallation

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The alkylation of [Ru(tp)Cl(cod)] (**1**) (tp=hydrotris(pyrazolyl)borate) with AlR_3 (R=Et, Me) successfully proceeded in a benzene or toluene solution at room temperature to give the corresponding [Ru(tp)R(cod)] complexes (R=Et (**2**), Me (**4**)) in high yields (82 and 96%, respectively). On the other hand, the reaction of **1** with an ethylmagnesium compound (Et_2Mg or EtMgBr) or EtLi provided a significant amount of [Ru(tp)H(cod)] (**3**) together with **2**.

Hydrotris(pyrazolyl)borates ($tp^- = [BH(pz)_3]^-$) are an important class of tridentate ligands in coordination chemistry.[1] Recently, these ligands have been extensively used in organometallic chemistry with the expectations of the novel reactivities and structures of tp-coordinated organometallic compounds, originating from the unique coordination and electronic properties of tp ligands.[2—4] One of the most common reactions of synthesizing organometallic compounds is transmetallation. This reaction is also important as an elementary step of catalytic processes. However, most of the tp-coordinated organotransition metals so far reported have been prepared by an anionic ligand displacement of the parent organotransition metals with tp^-M^+ salts (M = Na, K, Tl), and to the best of our knowledge only four examples of synthesis by transmetallation have been reported.[4] In this study we examined the alkylation of tp-coordinated ruthenium(II) chloride with several metal alkyls of the main-group elements, and found that trialkylaluminums served as particularly efficient alkylating agents.

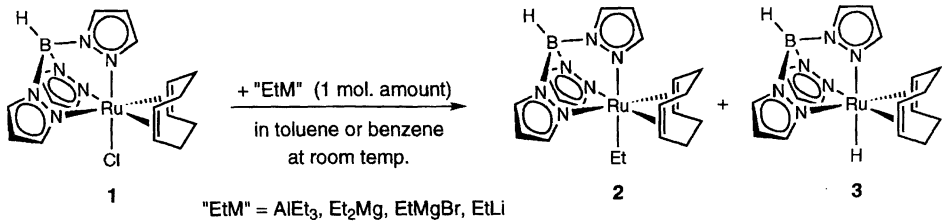
Results and Discussion

[Ru(tp)Cl(cod)] (cod = 1,5-cyclooctadiene) (**1**)[2c] was treated with metal ethyls of the main-group elements in a toluene or benzene solution (Scheme 1). The reactions proceeded readily at room temperature (< 30 min) irrespective of the metal ethyls employed, giving a mixture of ethyl- and hydridoruthenium complexes, [Ru(tp)Et(cod)] (**2**) and [Ru(tp)H(cod)] (**3**),[5] respectively. It has been noted that the selectivity of the reaction varies significantly with the kinds of metal ethyls (Table 1). The highest selectivity for the formation of **2** (88%) was observed with $AlEt_3$ (Entry 1). In this case, ethyl complex **2** was isolated in 82% yield by column chromatography (Al_2O_3/hexane). On the other hand, the reactions using EtLi and ethylmagnesiums (Et_2Mg and EtMgBr) afforded significant amounts of hydride complex **3** and an unidentified tp-containing species together with **2** (Entries 2—5). For example, the treatment of **1** with Et_2Mg in benzene at room temperature provided **2**, **3**, and an unidentified species in a 32 : 48 : 20 ratio (Entry 2). Furthermore, in the reaction with Et_2Mg under refluxing benzene, no formation of **2** was observed and **3** was obtained in 33% selectivity

Table 1. Reactions of [Ru(tp)Cl(cod)] (**1**) with Metal Ethyls of the Main Group Elements[a]

Entry	Metal ethyl	Product ratio[b]		
		2	**3**	Others[c]
1	Et_3Al	88	12	0
2	Et_2Mg	32	48	20
3[d]	Et_2Mg	0	33	67
4	EtMgBr	53	47	Trace
5	EtLi	34	34	32

a) All reactions were run with equimolar amounts of **1** and metal ethyls in a toluene or benzene solution at room temperature unless otherwise noted. b) Determined by ^{1}H NMR analysis of crude products. c) See text. d) The reaction was performed in reflux benzene.



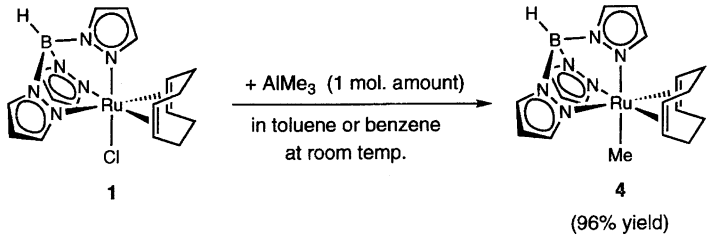
Scheme 1.

together with free pyrazol, which may be formed by the degradation of tp (Entry 3).

The preparation of [Ru(tp)Me(cod)] (**4**) was also successful using $AlMe_3$ as an alkylating agent (96% isolated yield) (Scheme 2). Although complex **4** was also produced by the reactions of **1** with methylmagnesium compounds (Me_2Mg and MeMgBr), its isolation was unsuccessful due to contamination by unidentified tp species.

Complexes **2** and **4** were characterized by NMR spectroscopy and elemental analysis. The NMR data are listed in Table 2. As expected from the reported data for tp-coordinated organoruthenium(II)[2] and organopalladium[6] complexes, the methylene protons of the ethyl group in **2** and the methyl protons in **4** appeared at considerably low magnetic fields in the ^{1}H NMR spectra ($\delta = 2.91$ and 1.82, respectively), reflecting the cationic nature of the ruthenium center. The ^{1}H and ^{13}C NMR signals of the pyrazolyl groups were observed as two distinct sets of resonances in a 2 : 1 ratio for both complexes, indicating the C_s symmetry within the molecules. The cod ligand also exhibited signals consistent with the C_s symmetry.

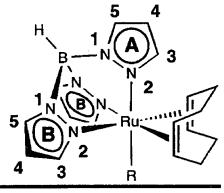
We found in this study that the selectivity for ethyl com-



1 **4** (96% yield)

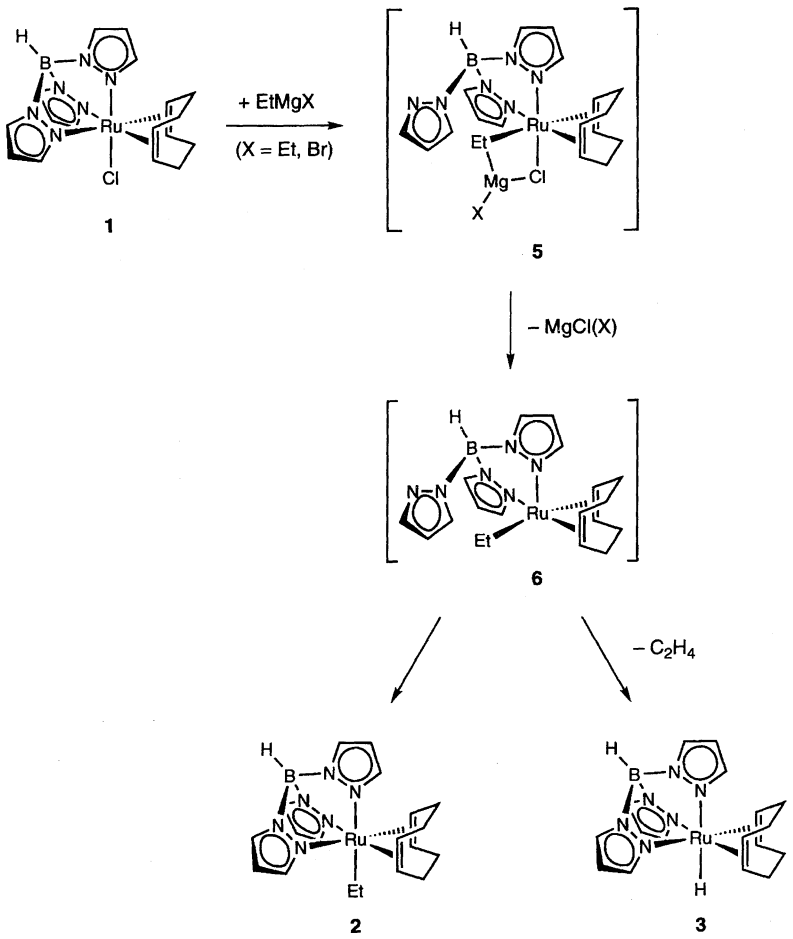
Scheme 2.

Table 2. NMR Data for [Ru(tp)R(cod)] Complexes (**2**, **4**)[a]

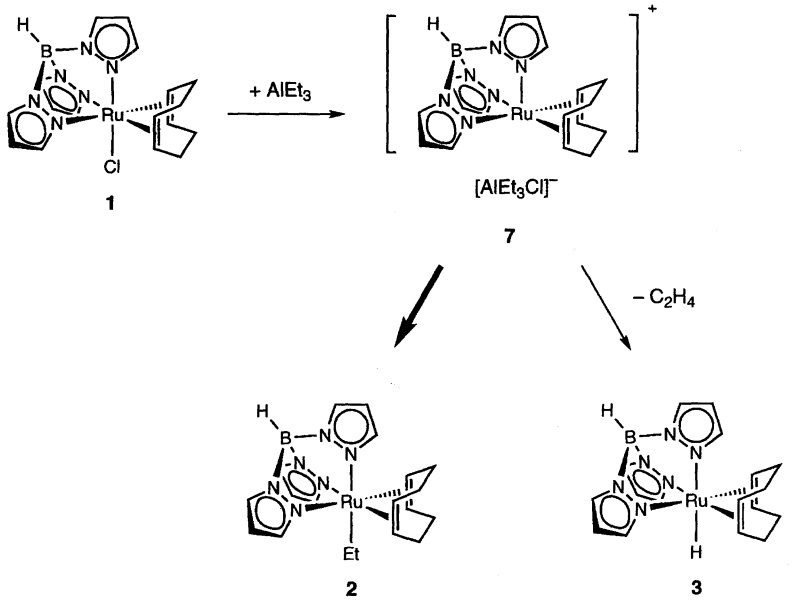


Complex	^{1}H NMR			^{13}C NMR		
	δ	J_{HH}	Assignment	δ	J_{CH}	Assignment
2 (R=Et)	0.44 (t, 3H)	7.6	$RuCH_2CH_3$	16.9	122	$RuCH_2CH_3$
	1.86 (d, 2H)	8.8	cod	24.7	135	$RuCH_2CH_3$
	1.91 (d, 2H)	8.3	cod	30.2	127	cod
	2.51 (m, 4H)		cod	75.9	159	cod
	2.91 (q, 2H)	7.6	$RuCH_2CH_3$	82.5	155	cod
	3.29 (m, 4H)		cod	105.5	177	$C_B{}^4$
	5.83 (t, 2H)	2.2	$H_B{}^4$	105.6	177	$C_A{}^4$
	6.04 (t, 1H)	2.2	$H_A{}^4$	134.7	185	$C_B{}^5$
	7.05 (d, 2H)	2.0	$H_B{}^3$	135.4	187	$C_A{}^5$
	7.38 (d, 2H)	2.0	$H_B{}^5$	139.3	184	$C_B{}^3$
	7.50 (d, 1H)	2.4	$H_A{}^5$	143.0	184	$C_A{}^3$
	8.13 (d, 1H)	2.0	$H_A{}^3$			
4 (R=Me)	1.82 (s, 3H)		$RuCH_3$	1.4	119	$RuCH_3$
	1.82 (d, 2H)	8.3	cod	30.2	125	cod
	1.88 (d, 2H)	8.3	cod	30.4	125	cod
	2.50 (m, 2H)		cod	74.7	156	cod
	2.59 (m, 2H)		cod	82.1	154	cod
	3.23 (m, 2H)		cod	105.7	177	$C_B{}^4$
	3.35 (m, 2H)		cod	105.7	177	$C_A{}^4$
	5.83 (t, 2H)	2.2	$H_B{}^4$	134.5	185	$C_B{}^5$
	6.09 (t, 1H)	2.2	$H_A{}^4$	135.6	189	$C_A{}^5$
	7.07 (d, 2H)	2.0	$H_B{}^3$	139.2	185	$C_B{}^3$
	7.35 (d, 2H)	2.4	$H_B{}^5$	143.2	184	$C_A{}^3$
	7.54 (d, 1H)	2.4	$H_A{}^5$			
	8.21 (d, 1H)	2.0	$H_A{}^3$			

a) In C_6D_6, at room temperature. Coupling constants are reported in Hz.



Scheme 3.



Scheme 4.

plex **2** varies significantly with the kinds of ethylating agents (Table 1). A possible route to hydride complex **3** involves a β-hydrogen elimination of **2** generated in the reaction systems. However, isolated **2** was found to be fairly stable in solution; no decomposition took place in pure benzene, even at 80 °C for several hours. Furthermore, no formation of **3** was observed when **2** was treated with Et_2Mg in benzene. Therefore, a β-hydrogen elimination giving **3** is considered

to occur during the transmetallation of **1** with metal ethyls.

The transmetallation of **1** with ethylmagnesium compounds, EtMgX (X = Et, Br), may proceed by a four-center mechanism, in which the ruthenium and magnesium metals are doubly bridged by the exchanging ligands (Cl and Et) (Scheme 3).[7] Since the starting complex **1** is a coordinatively saturated, 18-electron species, the formation of a bridged intermediate **5** must involve the dissociation of one of the ligands in **1**, most probably the pyrazolyl ligand.[8] Therefore, after the elimination of magnesium chloride from **5**, the resulting ethylruthenium species **6** should be coordinatively unsaturated, and, thereby, it is liable to undergo β-hydrogen elimination, affording hydride **3**, and a further decomposition, giving unidentified tp species. A similar situation is expected in the transmetallation of **1** with EtLi. In this case, the involvement of an ionic ruthenium intermediate $Li^+[Ru(tp)Et(Cl)(cod)]^-$ is more plausible than a bridged intermediate, like **5**.

Unlike the magnesium and lithium ethyls, triethylaluminum may serve as a Lewis acid, and tends to abstract an anionic ligand from a transition metal center.[7,9] Therefore, it seems convincing that the reaction of **1** with $AlEt_3$ initially forms a cationic $[Ru(tp)(cod)]^+$ species having a chlorotriethylaluminate anion (**7**) (Scheme 4). In this species, the ruthenium moiety is already coordinatively unsaturated without the dissociation of the pyrazolyl ligand, and thereby may directly form the coordinatively saturated ethylruthenium complex **2** by an interaction with $[AlEt_3Cl]^-$. The overall processes would provide a situation less prone to cause β-hydrogen elimination and further decomposition.

In summary, we have succeeded for the first time to synthesize tp-coordinated alkylruthenium complexes by transmetallation. The use of alkylaluminums provides quite clean reaction systems to give alkylruthenium complexes in high yields.

Experimental

General. All of the manipulations were carried out under a nitrogen atmosphere using conventional Schlenk techniques. Nitrogen gas was dried by passing through P_2O_5 (Merck, SICAPENT). The NMR spectra were recorded on a JEOL JNM-A400 spectrometer (^{1}H NMR, 399.65 MHz; ^{13}C NMR, 100.40 MHz). The chemical shifts are reported in δ ppm referred to an internal $SiMe_4$ standard.

Diethyl ether, benzene, toluene, and hexane were dried over sodium benzophenone ketyl and distilled just before use. Benzene-d_6 and toluene-d_8 were dried over $LiAlH_4$ and vacuum transferred and stored under a nitrogen atmosphere. Hydrotris(pyrazolyl)borate[10] and [Ru(tp)Cl(cod)][2c] were synthesized according to the literature. All other compounds used in this study were used as obtained from commercial sources.

Preparation of [Ru(tp)Et(cod)] (2). Entry 1 in Table 1. A toluene solution of $AlEt_3$ (2.67 M, 25.0 μl, 0.0668 mmol) was added to an orange solution of [Ru(tp)Cl(cod)] (**1**) (30.0 mg, 0.0655 mmol) in toluene (5 ml) at room temperature. The color of the solution quickly turned yellow. The solution was stirred for 1 h and diluted with ether (2 ml). A small quantity of dark-gray solid was precipitated in the system. The heterogeneous mixture was filtered through a filter-paper-tipped cannula, and the residue was washed with benzene (5 ml). The combined filtrates were concentrated to dryness to give a mixture of **2** and **3** (29.3 mg, **2** : **3** = 88 : 12 (^{1}H NMR)).[5] The crude product was purified by column chromatography on 10% Al_2O_3 using hexane as the eluent (R_f = 0.58) to give a pale-yellow solid of **2** (24.2 mg, 82%). Found: C, 51.34; H, 6.25%. Calcd for $C_{19}H_{27}N_6BRu$: C, 50.56; H, 6.03%.

Preparation of [Ru(tp)Me(cod)] (3). A toluene solution of $AlMe_3$ (2.36 M, 28.0 μl, 0.0661 mmol) was added to an orange solution of **1** (30.0 mg, 0.0655 mmol) in toluene (5 ml) at room temperature. The mixture was stirred for 1 h, and then diluted with ether (2 ml). A small amount of dark-gray precipitate generated in the system was removed by filtration, and the filtrate was concentrated to dryness. The crude product was dissolved in hexane, filtered though a short Celite column, and concentrated to dryness to yield 27.5 mg (96%) of **3** as a pale-yellow solid. Found: C, 49.04; H, 5.85%. Calcd for $C_{18}H_{25}N_6BRu$: C, 49.44; H, 5.76%.

Reaction of [Ru(tp)Cl(cod)] (1) with Et_2Mg or EtMgBr. (a) Entry 2 in Table 1. A typical procedure for the reaction of **1** with EtMgX (X = Et or Br, Entry 2—4) is as follows. An ethereal solution of Et_2Mg (0.663 M, 51.3 μl, 0.0340 mmol) was added to an orange solution of [Ru(tp)Cl(cod)] (15.6 mg, 0.0341 mmol) in benzene (3 ml) at room temperature. The color of the solution quickly turned yellow. The mixture was stirred for 1 h and then diluted with ether (2 ml). A small quantity of dark-gray solid was precipitated in the system. The heterogeneous mixture was filtered through a filter-paper-tipped cannula and the residue was washed with benzene (5 ml). The combined filtrates were concentrated to dryness to give a mixture of **2**, **3**, and an unidentified tp-containing by-product (17.2 mg, **2** : **3** : by-product = 32 : 48 : 20 (^{1}H NMR)).

(b) Entry 3 in Table 1. The reaction of **1** (50.0 mg, 0.109 mmol) with an ethereal solution of Et_2Mg (0.650 M, 168 μl, 0.109 mmol) in refluxing benzene (8 ml) gave a mixture of **3** and pyrazol after the workup-procedure described above (42.5 mg, **3** : pyrazol = 33 : 67 (^{1}H NMR)).

(c) Entry 4 in Table 1. The reaction of **1** (2.57 mg, 0.0056 mmol) with an etheal solution of EtMgBr (1.30 M, 5.0 μl, 0.0062 mmol) in benzene-d_6 (0.4 ml) at room temperature gave a mixture of **2**, **3**, and a trace amount of by-product after the workup-procedure described above (1.70 mg, **2** : **3** = 53 : 47 (^{1}H NMR)).

Reaction of [Ru(tp)Cl(cod)] (1) with EtLi. Entry 5 in Table 1. A solid of EtLi (2.6 mg, 0.0722 mmol) was placed in a Schlenk tube. After a solution of **1** (33.1 mg, 0.0723 mmol) in benzene (3 mL) was added, the mixture was stirred for 1 h at room temperature. A small quantity of white solid was precipitated in the system. The mixture was filtered through a filter-paper-tipped cannula and the residue was washed with benzene (5 ml). The combined filtrates were concentrated to dryness to give a mixture of **2**, **3**, and an unidentified tp-containing by-product (21.9 mg, **2** : **3** : by-product = 34 : 34 : 32 (^{1}H NMR)).

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References

1) S. Trofimenko, *Chem. Rev.*, **93**, 943 (1993).

2) Precedents of organoruthenium complexes having tp ligands: a) N. W. Alcock, A. F. Hill, and R. P. Melling, *Organometallics*, **10**, 3898 (1991); b) A. F. Hill, *J. Organomet. Chem.*, **395**, C35 (1990); c) F. A. Jalon, A. Otero, and A. Rodriguez,

J. Chem. Soc., Dalton Trans., **1995**, 1629; d) B. Moreno, S. Sabo-Etienne, and B. Chaudret, *J. Am. Chem. Soc.*, **116**, 2635 (1994); e) M. O. Albers, S. F. A. Crosby, D. C. Liles, D. J. Robinson, A. Shaver, and E. Singleton, *Organometallics*, **6**, 2014 (1987); f) A. M. McNair, D. C. Boyd, and K. R. Mann, *Organometallics*, **5**, 303 (1986); g) M. O. Albers, D. J. Robinson, A. Shaver, and E. Singleton, *Organometallics*, **5**, 2199 (1986), and references cited therein.

3) Recent examples of tp-coordinated organotransition metal complexes other than ruthenium: S. A. O'Reilly, P. S. White, and J. L. Templeton, *J. Am. Chem. Soc.*, **118**, 5684 (1996); A. L. Canty, A. Dedieu, H. Jin, A. Milet, and M. K. Richmond, *Organometallics*, **15**, 2845 (1996); Y. Alvarado, P. J. Daff, P. J. Peres, M. L. Poveda, R. Sanchez-Delgado, and E. Carmona, *Organometallics*, **15**, 2192 (1996); J. M. Boncella, M. L. Cajigal, and K. A. Abboud, *Organometallics*, **15**, 1905 (1996); Y. D. Ward, L. A. Villanueva, G. D. Allred, S. C. Payne, M. A. Semones, and L. S. Liebeskind, *Organometallics*, **14**, 4132 (1995); F. J. Lalor; T. J. Desmond, G. M. Cotter, C. A. Shanahan, G. Ferguson, M. Parvez, and B. Ruhl, *J. Chem. Soc., Dalton Trans.*, **10**, 1709 (1995); A. M. LaPointe, R. R. Schrock, and W. M. Davis, *J. Am. Chem. Soc.*, **117**, 4802 (1995); A. A. Purwoko and J. Lees, *Inorg. Chem.*, **34**, 424 (1995); S. N. Brown and J. M. Mayer, *J. Am. Chem. Soc.*, **116**, 2219 (1994); S. G. Feng, P. S. White, and J. L. Templeton, *Organometallics*, **12**, 2131 (1993); J. H. MacNeil, A. W. Roszak, M. C. Baird, K. F. Preston, and A. L. Rheingold, *Organometallics*, **12**, 4002 (1993); T. R. Belderrain, E. Gutierrez, A. Monge, M. C. Nicasio, M. Paneque, M. L. Poveda, and E. Carmona, *Organometallics*, **12**, 4431 (1993); P. E. Bloyce, J. Mascetti, and A. Rest, *J. Organomet. Chem.*, **444**, 223 (1993); K. Ohkita, H. Kurosawa, T. Hasegawa, T. Shirafuji, and I. Ikeda, *Inorg. Chim. Acta*, **198-200**, 275 (1992), and references cited therein.

4) Precedents of tp-coordinated organotransition metal complexes prepared by transmetallation: A. Domingos, N. Marques, A. P. de Matos, I. Santos, and M. Silva, *Organometallics*, **13**, 654 (1994); L. Hasinoff, J. Takats, X. W. Zhang, A. H. Bond, and R. D. Rogers, *J. Am. Chem. Soc.*, **116**, 8833 (1994); J. Ipaktschi and W. J. Sulzbach, *J. Organomet. Chem.*, **426**, 59 (1992); D. L. Reger, M. E. Tarquini, and L. Lebioda, *Organometallics*, **2**, 1763 (1983).

5) Hydride complex **3** is a known compound,[2c—e] which has been identified based on the ^{1}H NMR data reported.

6) In tp-coordinated palladium complex [Pd(tp)MeEtPh], the methylene protons of ethyl group and the methyl protons show similar chemical shifts ($\delta = 2.83$ and 1.81, respectively): A. J. Canty, H. Jin, A. S. Roberts, B. W. Skelton, P. R. Traill, and A. H. White, *Organometallics*, **14**, 199 (1995).

7) For general discussions of the mechanisms of transmetallation, see: A. Yamamoto, "Organotransition Metal Chemistry: Fundamental Concepts and Applications," Wiley-Interscience, New York (1986).

8) Partial dissociation of tp ligand has been observed in some instances: E. Del Ministro, O. Renn, H. Rueegger, L. M. Venanzi, U. Burckhardt, and V. Gramlich, *Inorg. Chim. Acta*, **240**, 631 (1995); M. Cocivera, G. Ferguson, F. J. Lalor, and P. Szczecinski, *Organometallics*, **1**, 1139 (1982), and references cited therein.

9) For recent examples of formation of cationic species by the interaction of aluminum alkyls with transition metal complexes, see: J. J. Eisch, S. I. Pombrik, and G.-X. Zheng, *Organometallics*, **12**, 3856 (1993); J. J. Eisch, K. R. Caldwell, S. Werner, and C. Krüger, *Organometallics*, **10**, 3417 (1991), and references cited therein.

10) S. Trofimenko, *Inorg. Synth.*, **12**, 99 (1971).