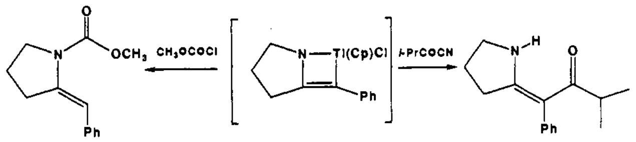
Scheme IV



9 (88 %) 3a 8 (81 %)

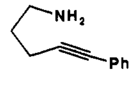
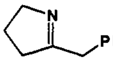
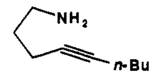
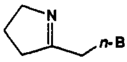
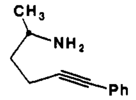
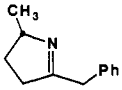
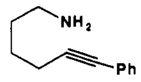
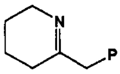
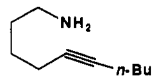
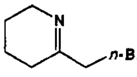
attempts to date to isolate and characterize bicyclic azatitanetines such as **3a** have been frustrated by the high reactivity of these species.[12]

Subsequent to these studies this cyclization procedure was extended to a range of representative alkynylamines (e.g., **1a**–**e**). That an analogous procedure could be utilized for the generation of mono Cp imidozirconium complexes was demonstrated by the treatment of $CpZr(CH_3)_2Cl$ (prepared in situ from $CpZrCl_3\cdot DME$[13] and 2 equiv of CH_3Li) with **1b** in THF at 25 °C to afford **4b** (82% isolated) after methanolysis. *It is of particular significance in a preparative context that the generation of $CpM(X){=}NR$ complexes from the precursors $CpM(CH_3)_2X$ and H_2NR proceeds rapidly at temperatures ≤25 °C.* By way of contrast, the corresponding reactions of hindered primary amines with $Cp_2Zr(CH_3)_2$ require 3 days at 85 °C to produce imidozirconocene complexes of the type $Cp_2Zr{=}NR$.[6a] Moreover, exposure of the relatively unhindered amine **1a** to $Cp_2Zr(CH_3)_2$ resulted in no appreciable reaction at 25 °C and only minimal reaction at higher temperatures (e.g., 80 °C, 24 h). *It is of particular interest that heteroannulations of the above variety can be readily effected using catalytic quantities of $CpTiCl_3$ at 25 °C* (Scheme III).

The synthetic generality of this new transition metal based method for heteroannulation was subsequently tested by its application to the construction of a variety of representative ring systems (Table I).[14]

The reactive azametalletines **3** formed as intermediates in stoichiometric cyclization reactions could be *selectively* functionalized on carbon or nitrogen by the use of appropriate carbon-centered electrophiles. Accordingly, treatment of representative azametalletines (e.g., **3a**) with acyl cyanides[15] or nitriles gave rise to exclusive functionalization at carbon, leading to the formation of vinylogous amides (e.g., **8**) or vinylogous amidines [(e.g., **7** (vide infra)], respectively. By way of contrast, acylation of azametalletines with acyl chlorides led to selective functionalization at nitrogen to provide enamides such as **9** (Scheme IV).

Table I

substrate **1**	product **4**	procedure[a]	yield, %
a. 		A B C	94 96 83
b. 		A B C	94 94 82
c. 		B C	92 77
d. 		C D	69 88
e. 		C D	74 89

[a] A: 20 mol % $CpTiCl_3$, 40 mol % $i\text{-}Pr_2NEt$, THF, 25 °C. B: $CpTi(CH_3)_2Cl$, THF, 25 °C. C: $CpZr(CH_3)_2Cl$, THF, 25 °C. D: 20 mol % $CpTiCl_3$, 40 mol % $PhN(CH_3)_2$, C_7H_8, 80 °C.

The foregoing examples provide a concise illustration of the synthetic potential of this new approach to heterocycle annulation. The utilization of this novel heteroannulation procedure for the synthesis of representative indolizidine alkaloids[16] as well as related naturally occurring ring systems will be described in future accounts from these laboratories.

Acknowledgment. Support for this research by grants from the Alfred P. Sloan Foundation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation is gratefully acknowledged.

Supplementary Material Available: Listings of spectroscopic and analytical data for the compounds **1a**–**e**, **4a**–**e**, and **7**–**9** (7 pages). Ordering information is given on any current masthead page.

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(12) This is not surprising in that the only reported examples of isolable group IV metalletines are derived from the reaction of imidozirconocene complexes that possess a bulky R group on nitrogen with diphenylacetylene.[6a] Attempts to directly characterize the adduct **6** by ^1H NMR spectroscopy were complicated by the presence of trace amounts of paramagnetic impurities.

(13) Lund, E. C.; Livinghouse, T. *Organometallics* **1990**, *9*, 2426.

(14) A representative experimental procedure is as follows for **3,4-dihydro-5-benzyl-2*H*-pyrrole** (**4a**). **Method A**: To $CpTiCl_3$ (44 mg, 0.2 mmol) in THF (3 mL) was added $i\text{-}Pr_2NEt$ (70 μL, 0.4 mmol) followed by dropwise addition of a solution of **1a** (159 mg, 1 mmol) in THF (2 mL). After 30 min, a few drops of 5% methanolic NaOH were added, and the reaction mixture was taken to dryness. The solids were triturated with hexane, and the organic phase was filtered through powdered K_2CO_3. Concentration of the organic phases afforded 149 mg (94%) of **4a** as the sole reaction product. **Method B**: To $CpTiCl_3$ (219 mg, 1 mmol) in THF (3 mL) at 0 °C was added CH_3Li (1.4 M in Et_2O, 1.43 mL, 2 mmol). The reaction mixture was warmed to 25 °C over 15 min, and **1a** (159 mg, 1 mmol) in THF (2 mL) was added dropwise over 5 min. After 1 h, 5% methanolic NaOH (0.5 mL) was carefully added, and the reaction mixture was taken to dryness. Trituration with hexane, followed by filtration through powdered K_2CO_3 and concentration afforded **4a** in 96% yield. In cases where filtration through K_2CO_3 was not sufficient, the product was filtered through a small plug of silica (1:1 Et_2O–hexane). **Method C**: To $CpZrCl_3\cdot DME$ (176 mg, 0.5 mmol) suspended in THF (1.5 mL) maintained at 0 °C was added CH_3Li (1.4 M in Et_2O, 0.71 mL, 1 mmol). After 1.5 h, the reaction mixture was warmed to 25 °C, and **1a** (80 mg, 0.5 mmol) in THF (0.4 mL) was added. After 10 min the reaction mixture was diluted with hexane, stirred for 20 min, and then allowed to settle. The organic phase and one 1:1 Et_2O–hexane wash of the solids were filtered through silica gel and concentrated to give **4a** (66 mg, 83%): ^1H NMR (300 MHz, $CDCl_3$) δ 7.25 (m, 5 H, Ph), 3.83 (m, 2 H, NCH_2), 3.68 (s, 2 H, $PhCH_2$), 2.39 (m, 2 H, $N{=}CCH_2$), 1.83 (m, 2 H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.56, 137.12, 129.02, 128.57, 126.57, 61.05, 40.75, 36.53, 22.29; IR (film) 3100–2850, 1604, 1496 cm^{-1}; high-resolution mass spectrum calcd for $C_{11}H_{13}N$ (M^+) 159.1048, found 159.1046.

(15) Hunig, S.; Schaller, R. *Angew Chem., Int. Ed. Engl.* **1982**, *21*, 36.

(16) McGrane, P. L.; Livinghouse, T. *J. Org. Chem.* **1992**, *57*, 1323.

Group-Transfer Polymerization Using Cationic Zirconocene Compounds

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Received January 2, 1992

The chemistry of cationic metallocene compounds (e.g, **1**) of the group 4 transition elements has attracted recent attention; such compounds function as useful models for the catalytic intermediates involved in Ziegler–Natta (Z–N) polymerization and hydrogenation of simple olefins.[1] These compounds have also been shown to be potentially useful in organic synthesis. For example, such compounds function as catalysts for the preparation of substituted pyridines,[2] and related heteroatom derivatives function

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(1) For leading references, see: (a) Jordan, R. F.; Bajgur, C. S. *J. Am. Chem. Soc.* **1986**, *108*, 7410. (b) Bochmann, M.; Wilson, L. M. *J. Chem. Soc., Chem. Commun.* **1986**, 1610. (c) Jordam R. F.; LaPointe, R. E.; Bajgur, C. S.; Echols, S. F.; Willett, R. *J. Am. Chem. Soc.* **1987**, *109*, 4111. (d) Bochmann, M.; Wilson, L. M.; Hursthouse, M. B.; Short, R. L. *Organometallics* **1987**, *6*, 2556. (e) Jordan, R. F. *J. Chem. Educ.* **1988**, *65*, 285. (f) Hlatky, G. G.; Turner, H. W.; Eckman, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 2728. (g) Jordan, R. F.; LaPointe, R. E.; Bradley, P. K.; Baenziger, N. *Organometallics* **1989**, *8*, 2892. (h) Jordan, R. F.; LaPointe, R. E.; Baenziger, N.; Hinch, G. D. *Ibid* **1990**, *9*, 1539. (i) Park, J. W.; Henling, L. M.; Schaefer, W. P.; Grubbs, R. H. *Ibid.* **1990**, *9*, 1650.

(2) Jordan, R. F.; Taylor, D. F.; Baenziger, N. C. *Organometallics* **1990**, *9*, 1546 and references cited therein.

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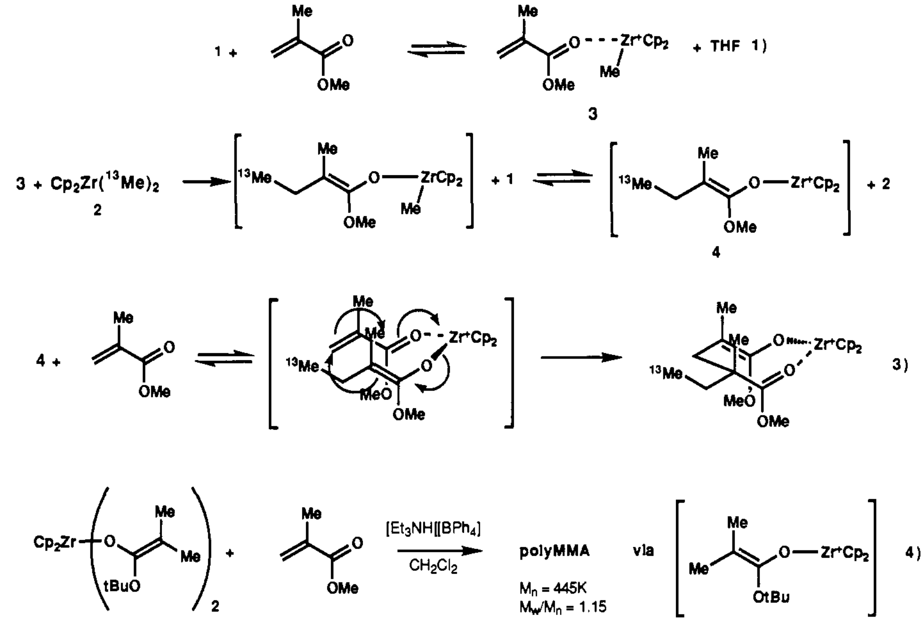
Table I. Polymerization of Methyl Methacrylate with Compounds **1** and **2**[a]

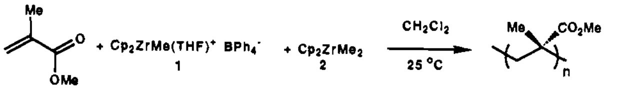
entry	[**1**] (mM)	[**2**] (mM)	[MMA] (M)	*T* (°C)	time (min)	% conversion	M_n[b]	M_w/M_n	[Zr*]/[**1**][c]
1[d]	7.5	24.3	3.10	25	15	100.0	93 000	1.40	0.444
2[d]	7.5	24.3	3.10	0	40	100.0	149 200	1.32	0.277
3[d,e]	7.5	24.3	3.10	0	60	7.2	113 000	1.39	0.054
4[f]	6.3	20.0	2.61	0	10	2.2	62 900	1.19	0.015
5[f]	6.2	20.0	2.61	0	15	7.8	77 600	1.19	0.042
6[f]	6.2	20.0	2.61	0	20	17.6	88 800	1.28	0.083
7[f]	6.2	20.0	2.61	0	30	37.5	130 200	1.39	0.121
8[f]	6.2	20.0	2.61	0	40	95.0	158 300	1.33	0.253

[a] All reactions were conducted in CH_2Cl_2 solution under the conditions shown, except where indicated. [b] Determination by GPC using monodisperse polyMMA standards. [c] Fraction of compound **1** that was involved in growing polymer chains was calculated according to the following formula: $([MMA]_0 \times \%\ \text{conversion})/([\mathbf{1}]_0 \times M_n)$. [d] Injection of a solution of compound **2** into a mixture of monomer and compound **1**. [e] The polymerization was conducted in THF. [f] Injection of a solution of compounds **1** and **2** into the monomer.

Scheme I



as catalysts for the Diels–Alder reaction.[3] We report here an unexpected reaction of such compounds; they serve as excellent catalysts for the polymerization of methyl methacrylate in the presence of neutral metallocenes (e.g., **2** in the following equation).



The poly(methyl methacrylate) produced in these polymerizations is predominantly syndiotactic (80% r diads at 0 °C) with a microstructure consistent with a chain-end control mechanism for propagation [2(m)(r)/(mr) = 0.88].[4] The polymers possess narrow molecular weight distributions (M_w/M_n = 1.2–1.4, Table I), and the molecular weights increase with decreasing temperature of polymerization (e.g., entries 1 and 2). We attribute this to the less efficient generation of active catalyst (vide infra) at lower temperatures (Table I, last column). Donor solvents decrease the rate of polymerization, and a higher molecular weight polymer is produced with a broader molecular weight distribution at the same degree of conversion (compare entry 3 vs 5).

The degree of polymerization was studied as a function of conversion. As shown in Table I, entries 4–8, there is a significant induction period.[5] One can estimate that only a small fraction of compound **1** (or compound **2**) that is present initiates growing polymer chains and that the number of actively growing chains increases with increasing conversion (Table I, last column); this leads to the production of a high molecular weight polymer and a nonlinear relationship between molecular weight and conversion.

The intimate details of the mechanism of this process are of considerable interest. Similar polymerizations of methyl methacrylate using organolanthanide(III) catalysts have been reported recently and may be mechanistically related to the process described here.[6]

Compound **2** is responsible for initiation; the use of $Cp_2Zr(^{13}CH_3)_2$ resulted in the incorporation of a labeled methyl group into the polymer. Two signals in the ^{13}C NMR spectrum of the polymer consistent with that of methyl group of the $C(CH_3)(CO_2Me)CH_2{}^{13}CH_3$ moiety were detected (see the supplementary material).[7] Furthermore, the degree of polymerization determined from the ^{13}C NMR spectrum of labeled polymer (M_n = 69 500) was in good agreement with that determined by GPC (63 500); each polymer chain was evidently initiated by compound **2**.

We wish to propose that the mechanism of this polymerization is as shown in Scheme I. The species responsible for propagation is believed to be cationic zirconium enolate **4**, derived from isomerization of methacrylate complex **3**,[8] a process which is facilitated by neutral metallocene **2** (see Scheme I). Propagation

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(3) Collins, S.; Koene, B. E.; Ramachandran, R.; Taylor, N. J. *Organometallics* **1991**, *10*, 2092.

(4) Bovey, F. A.; Tiers, G. V. D. *J. Polym. Sci.* **1960**, *44*, 173.

(5) There are a number of possible explanations for this behavior. See, for example, ref 9 and the following: (a) Penczek, S.; Kubisa, P.; Szymanski, R. *Makromol. Chem., Rapid Commun.* **1991**, *12*, 77. (b) Szwarc, M. *Ibid.* **1990**, *11*, 589. For a recent review of anionic/living polymerizations, see: Van Beylen, M.; Bywater, S.; Smets, G.; Szwarc, M.; Worsfold, D. J. *Adv. Polymn. Sci.* **1988**, *86*, 87.

(6) Yasuda, H.; Yamamoto, H.; Yokota, K.; Nakamura, A.; Miyake, S. *Shokubai* **1990**, *32*, 412 (cf. *Chem. Abstr.* **1991**, 114 (8), 62811w).

(7) The appearance of two signals is tentatively attributed to methyl end groups adjacent to meso and racemic dyads in the polymer. Their ratio is approximately consistent with the total dyad composition of the polymer.

(8) Complex formation between methyl methacrylate and $[Cp^*_2Zr(THF)Me][BPh_4]$ was observed at room temperature (see the supplementary material).

is postulated to occur via intramolecular Michael reaction between the cationic enolate **4** and additional, coordinated monomer. The propagation step is analogous to that postulated to occur in group-transfer polymerization of acrylates, initiated by enol silanes in the presence of, for example, Lewis acid catalysts.[9]

Indirect evidence for the intermediacy of enolate **4** is based on the following observations. A mixture of compound **1** and $Cp_2Zr(OCH{=}CMe_2)Me$[10a] gives rise to compound **2** at the expense of both starting materials (Scheme I, eq 2), and this mixture is active for polymerization. The bis enolate complex, $Cp_2Zr[OC(OtBu){=}CMe_2]_2$,[10b] in the presence of 1 equiv of a proton source ($[Et_3NH][BPh_4]$),[10c] rapidly polymerizes methyl methacrylate (eq 4, Scheme I: 96% conversion after 30 min at 0 °C; $M_n = 442000$, $M_w/M_n = 1.14$).

It is clear that the process described here is an efficient method for effecting high-conversion polymerization of methacrylate monomer to high molecular weight polymers with narrow molecular weight distributions. Work that is already in progress is designed to provide concrete evidence for the intermediacy of cationic enolate **4**, to investigate the kinetics of this process, and to evaluate whether polymer chains generated in this manner are living.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support of this work. D.G.W. also thanks Polysar Rubber Corporation for a generous stipend.

Supplementary Material Available: Experimental details for the preparation of relevant compounds, polymerizations, and polymer characterization including GPC analyses (18 pages). Ordering information is given on any current masthead page.

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[9] See, inter alia: (a) Webster, O. W. *Science* **1991**, *251*, 887. (b) Muller, A. H. E. *Makromol. Chem., Macromol. Symp.* **1990**, *32*, 87. (b) Sogah, D. Y.; Hertler, W. R.; Webster, O. W.; Cohen, G. M. *Macromolecules* **1987**, *20*, 1473. (c) Reetz, M. T.; Ostarek, R.; Piejko, K.-E.; Arlt, D. A.; Bomer, B. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1108. (d) Hertler, W. R.; Sogah, D. Y.; Webster, O. W.; Trost, B. M. *Macromolecules* **1984**, *17*, 1417.

[10] (a) Curtis, M. D.; Thanedar, S.; Butler, W. M. *Organometallics* **1984**, *3*, 1855. (b) See the supplementary material for the preparation and characterization of this compound. (c) Reaction of this compound with $[Et_3NH][BPh_4]$ in CD_2Cl_2 or THF-d_8 in the absence of monomer leads to the rapid appearance of a new species whose spectral features are consistent with a cationic enolate (see the supplementary material).

Regioselective C–N Bond Cleavage in an η^2(N,C)-Coordinated Pyridine and an η^1(N) → η^2(N,C) Bonding Rearrangement in Coordinated Quinoline: Models for Hydrodenitrogenation Catalysis

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The catalytic removal of sulfur and nitrogen from petroleum feedstocks and coal-derived liquids is essential to preclude the poisoning of hydrocracking and reforming catalysts and to reduce emissions of their oxides.[1] Industrial hydrodenitrogenation (HDN) is typically effected over sulfided $CoMo/Al_2O_3$ or $NiMo/Al_2O_3$ under conditions which remove nitrogen as NH_3.[2,3] The nitrogen-containing compounds which are most difficult to process are the aromatic heterocycles such as pyridine, quinoline, and indole derivatives.[2,4] One central question in HDN catalysis which remains unresolved concerns how the strong C–N bonds in these heterocycles are cleaved.[5] Herein we provide evidence for an η^1(N) → η^2(N,C) bonding rearrangement in model HDN substrates and demonstrate that nucleophilic attack of an η^2(*N*,*C*)-pyridine results in facile, regioselective C–N bond cleavage.

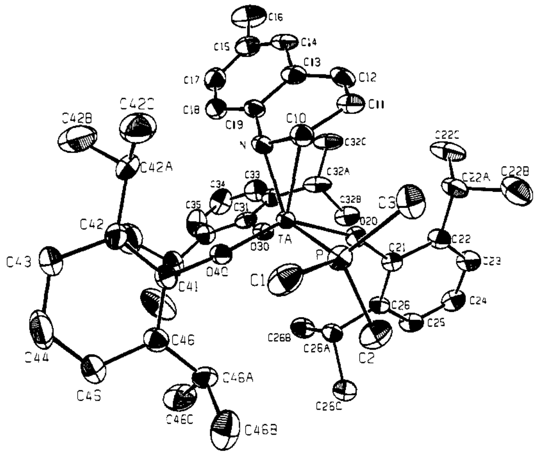

Figure 1. Molecular structure of (η^2(*N*,*C*)-6-methylquinoline)Ta(DIPP)$_3$(PMe$_3$) (**5**) (DIPP = O-2,6-$C_6H_3{}^iPr_2$). Selected interatomic distances (Å): Ta–N = 1.961 (7); Ta–C(10) = 2.208 (9); N–C(10) = 1.44 (1); C(10)–C(11) = 1.42 (1); C(11)–C(12) = 1.30 (1); C(12)–C(13) = 1.48 (2); C(13)–C(19) = 1.40 (1); N–C(19) = 1.41 (1). Selected bond angles (deg): Ta–N–C(19) = 145.0 (6); Ta–C(10)–C(11) = 123.4 (6); C(10)–Ta–N = 39.7 (3).

Upon reaction of $Ta(DIPP)_3Cl_2(OEt_2)$[6] (**1**, DIPP = O-2,6-$C_6H_3{}^iPr_2$) with 1 equiv of quinoline (QUIN), yellow (QUIN)Ta(DIPP)$_3$Cl$_2$ (**2**) is isolated in ca. 95% yield (Scheme I). The analogous 6-methylquinoline (6MQ) adduct, (6MQ)Ta(DIPP)$_3$Cl$_2$ (**3**), is prepared similarly. NMR data[7] for **2** and **3** are entirely consistent with the heterocycle bonding η^1(N) to the d^0 metal center. Upon reduction of (η^1(*N*)-QUIN)Ta(DIPP)$_3$Cl$_2$ (**2**) with 2 equiv of NaHg, a dark red, ***highly*** soluble compound is obtained, for which spectroscopic data suggest the formulation (η^2(*N*,*C*)-QUIN)Ta(DIPP)$_3$ (**4**). In particular, the quinoline H(2) resonance at δ 9.63 in the ^{1}H NMR spectrum of **2** has shifted upfield to δ 4.07 in complex **4** (both in C_6D_6), diagnostic of the η^2(N,C) bonding mode.[8-10]

The crystalline, 6-methylquinoline adduct (η^2(*N*,*C*)-6MQ)-Ta(DIPP)$_3$(PMe$_3$) (**5**) is afforded upon reducing **1** in the presence

---

[1] (a) Satterfield, C. N. *Heterogeneous Catalysis in Industrial Practice*; McGraw-Hill: New York, 1991. (b) Gates, B. C.; Katzer, J. R.; Schuit, G. C. A. *Chemistry of Catalytic Processes*; McGraw-Hill: New York, 1979.

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[3] For example, see: (a) Fish, R. H.; Michaels, J. N.; Moore, R. S.; Heinemann, H. *J. Catal.* **1990**, *123*, 74 and references therein. (b) Olalde, A.; Perot, G. *Appl. Catal.* **1985**, *13*, 373. (c) Satterfield, C. N.; Yang, S. H. *Ind. Eng. Chem. Process Des. Dev.* **1984**, *23*, 11. (d) Fish, R. H.; Thormodsen, A. D.; Moore, R. S.; Perry, D. L.; Heinemann, H. *J. Catal.* **1986**, *102*, 270.

[4] (a) Fish, R. H. *Ann. N.Y. Acad. Sci.* **1983**, *415*, 292. (b) Laine, R. M. *Ibid.* **1983**, *415*, 271. (c) Laine, R. M. *Catal. Rev.-Sci. Eng.* **1983**, *25*, 459 and references therein.

[5] For discussion, see refs 2 and 4 and the following: Vivier, L.; Dominguez, V.; Perot, G.; Kasztelan, S. *J. Mol. Catal.* **1991**, *67*, 267.

[6] Strickler, J. R.; Bruck, M. A.; Wexler, P. A.; Wigley, D. E. *Organometallics* **1990**, *9*, 266.

[7] Spectroscopic and analytical data for compounds **2–5** and **7** are available as supplementary material. Partial ^{1}H NMR (in C_6D_6) for 6MQ H(2) resonances: **3** (333 K) δ 9.24 (br); **5** (probe temperature) δ 3.68 (br s).

[8] (a) Covert, K. J.; Neithamer, D. R.; Zonnevylle, M. C.; LaPointe, R. E.; Schaller, C. P.; Wolczanski, P. T. *Inorg. Chem.* **1991**, *30*, 2494. (b) Neithamer, D. R.; Pârkányi, L.; Mitchell, J. F.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 4421.

[9] Smith, D. P.; Strickler, J. R.; Gray, S. D.; Bruck, M. A.; Holmes, R. S.; Wigley, D. E. *Organometallics* **1992**, *11*, 1275.

[10] For an η^1(N) → η^6(π) rearrangement in model ruthenium heterocycle compounds, see: (a) Fish, R. H.; Kim, H.-S.; Fong, R. H. *Organometallics* **1989**, *8*, 1375. (b) Fish, R. H.; Kim, H.-S.; Fong, R. H. *Ibid.* **1991**, *10*, 770.

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