Synthesis of 2-Transition-Metal-Substituted 1,3-Butadienyl Complexes with Unusual Structures and Facile Diels–Alder Reactions of Cobalt 1,3-Butadiene Complexes

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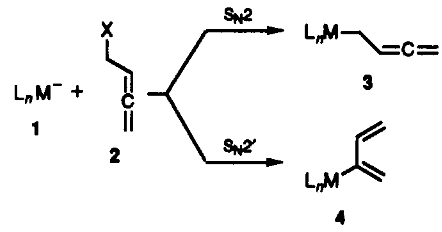
Summary: The cyclopentadienyliron dicarbonyl anion and (Rpy)(DMG)$_2$Co anions (R = H, t-Bu) react cleanly with 1,2-butadienyl chlorides and tosylates to generate transition-metal-substituted 1,3-butadienes. The cobalt-substituted 1,3-butadienes react under mild conditions and with high regioselectivity with a variety of dienophiles to yield transition-metal-substituted cyclohexenes. A variety of cyclohexanoid products can subsequently be obtained from these transition-metal-substituted cyclohexenes via demetalation reactions.

Over the last 15 years, several groups have been investigating organic applications of cycloaddition reactions between transition-metal complexes containing σ bonds to unsaturated ligands and electrophiles.[1] Along these lines, we were interested in preparing 4-transition-metal-substituted η^1-1,2-butadienyl complexes (**3**) and 2-transition-metal-substituted 1,3-butadienes (**4**) so that their reaction chemistry (particularly cycloaddition chemistry initially) could be investigated.

We envisioned that complexes of the form **3** and **4** could be prepared via reactions of transition-metal anions (**1**) with 1,2-butadienyl electrophiles (**2**). There are many examples of η^1-propargyl and η^1-allyl complex synthesis through reactions analogous to the S$_N$2 reaction[2] shown in Scheme I, and there are some examples of S$_N$2′ attack by transition-metal anions on propargyl and pentadienyl electrophiles.[3]

Scheme I



The allenyl electrophiles required for this work (**2b,c**) were prepared according to standard procedures from 1,2-butadien-4-ol (**2a**).[4] When 4-chloro-1,2-butadiene (**2b**) or 4-tosyl-1,2-butadiene (**2c**) was treated with CpFe(CO)$_2^-$Na$^+$ (**1a**),[5] (py)(DMG)$_2$Co$^-$Na$^+$ (**1b**),[6] or (4-*t*-Bupy)(DMG)$_2$Co$^-$Na$^+$ (**1c**), clean S$_N$2′ replacement of the leaving group by the transition metal occurred (Table I). Clean S$_N$2′ attack by the cobalt anion **1b** on propargyl bromide has been reported previously,[3d] so this outcome was not totally unexpected here. The iron-substituted butadiene **5** is a slightly air-sensitive and thermally sensitive red-orange oil which has been previously prepared by an alternative strategy.[1d,7] In contrast, cobalt-substituted diene complexes **6** and **7** are air-stable orange solids which have high thermal stability and can be prepared on a multigram scale from inexpensive starting materials.

On the basis of fact that related (py)(DMG)$_2$Co–isopropyl[8] and –neopentyl[9] complexes have large Co–C–C bond angles (114 and 130°, respectively), we suspected that steric interactions between the diene and DMG ligands in the cobalt diene complexes **6** and **7** might make the *s-cis* conformation of the diene more thermodynamically favorable than would normally be expected for 1,3-

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(1) For recent reviews of 3 + 2 cycloadditions involving transition-metal propargyl and allyl complexes see: (a) Welker, M. E. *Chem. Rev.* **1992**, *92*, 97. (b) Wojcicki, A. *Coord. Chem. Rev.* **1990**, *105*, 35. (c) Rosenblum, M. *J. Organomet. Chem.* **1986**, *300*, 191. Chan, D. M. T. In *Comprehensive Organic Syntheses*; Trost, B. M., Ed.; Pergamon Press: New York, 1991; Vol. 5, pp 271–314. For some recent examples of cycloadditions involving transition-metal complexes containing a σ bond to a dienyl ligand see: (d) Waterman, P. S.; Belmonte, J. E.; Bauch, T. E.; Belmonte, P. A.; Giering, W. P. *J. Organomet. Chem.* **1985**, *294*, 235. (e) Kuo, G.-H.; Helquist, P.; Kerber, R. C. *Organometallics* **1984**, *3*, 806. (f) Lee, G.-H.; Peng, S.-M.; Lush, S.-F.; Mu, D.; Liu, R.-S. *Organometallics* **1988**, *7*, 1155. (g) Lee, T.-W.; Liu, R.-S. *Organometallics* **1988**, *7*, 878. (h) Lee, G.-H.; Peng, S.-M.; Yang, G.-M.; Lush, S. F.; Liu, R.-S. *Organometallics* **1989**, *8*, 1106. (i) Yang, G.-M.; Lee, G.-H.; Peng, S.-M.; Liu, R.-S. *Organometallics* **1991**, *10*, 2531. (j) Wright, M. E.; Hoover, J. F.; Nelson, G. O.; Scott, C. P.; Glass, R. S. *J. Org. Chem.* **1984**, *49*, 3059. (k) Wright, M. E. *Organometallics* **1983**, *2*, 558.

(2) For a discussion of S$_N$2 reactions of transition-metal anions with 2-alkynyl and allyl electrophiles, see ref 1a and references therein.

(3) (a) Cooksey, C. J.; Dodd, D.; Johnson, M. D.; Lockman, B. L. *J. Chem. Soc., Dalton Trans.* **1978**, 1814. (b) Roustan, J.-L.; Cadiot, P. *C.R. Seances Acad. Sci., Ser. C* **1969**, *268*, 734. (c) Raseta, M. E.; Mishra, R. K.; Cawood, S. A.; Welker, M. E.; Rheingold, A. L. *Organometallics* **1991**, *10*, 2936. (d) Johnson, M. D.; Mayle, C. *J. Chem. Soc. D Commun.* **1969**, 192. (e) Foxman, B.; Marten, D.; Rosan, A.; Raghu, S.; Rosenblum, M. *J. Am. Chem. Soc.* **1977**, *99*, 2160. (f) Nesmeyanov, A. N.; Kolobova, N. E.; Zlotina, I. B.; Lokshin, B. V.; Leshcheva, I. F.; Znobina, G. K.; Anisimov, K. N. *J. Organomet. Chem.* **1976**, *110*, 339. (g) Kolobova, N. E.; Zlotina, I. B.; Solodova, M. Y. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*) **1977**, 2168. (h) Kolobova, N. E.; Zlotina, I. B.; Yudin, E. N. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*) **1978**, 588.

(4) Brandsma, L.; Verkruijsse, H. D. *Synthesis of Acetylenes, Allenes, and Cumulenes*; Elsevier: New York, 1981; pp 65, 171, 188.

(5) Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104.

(6) Schrauzer, G. N. In *Inorganic Syntheses*; Jolly, W. L., Ed.; McGraw-Hill: New York, 1968; Vol. XI, pp 61–70.

(7) (a) Bauch, T. E.; Giering, W. P. *J. Organomet. Chem.* **1976**, *114*, 165. (b) Bauch, T. E.; Konowitz, H.; Kerber, R. C.; Giering, W. P. *J. Organomet. Chem.* **1977**, *131*, C7. Two other iron diene complexes related to **5** have been prepared by alternative routes, but their reaction chemistry has not been reported: (c) Reger, D. L.; Belmore, K. A.; Mintz, E.; McElligott, P. J. *Organometallics* **1984**, *3*, 134. (d) Omrcen, T.; Conti, N. J.; Jones, W. M. *Organometallics* **1991**, *10*, 913.

(8) Marzilli, L. G.; Toscano, P. J.; Randaccio, L.; Bresciani-Pahor, N.; Calligaris, M. *J. Am. Chem. Soc.* **1979**, *101*, 6754.

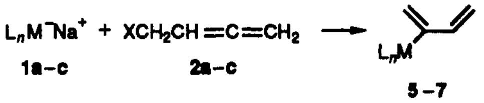
(9) Randaccio, L.; Bresciani-Pahor, N.; Toscano, P. J.; Marzilli, L. G. *J. Am. Chem. Soc.* **1981**, *103*, 6347.

0276-7333/93/2312-0998$04.00/0

Table I. Reactions of Transition-Metal Anions (1) with Allenyl Electrophiles (2)

entry no.	anion	electrophile	yield of diene complex, %
i	$CpFe(CO)_2$	**2b**	79
ii	$CpFe(CO)_2$	**2c**	92
iii	$(py)(DMG)_2Co$	**2b**	33
iv	$(py)(DMG)_2Co$	**2c**	75
v	$(4\text{-}t\text{-Bupy})(DMG)_2Co$	**2c**	58

Scheme II [a]



[a] Legend: L_mM = $CpFe(CO)_2$ (**1a**, **5**), $(py)(DMG)_2Co$ (**1b**, **6**), $(4\text{-}t\text{-Bupy})(DMG)_2Co$ (**1c**, **7**); X = OH (**2a**), Cl (**2b**), OTs (**2c**).

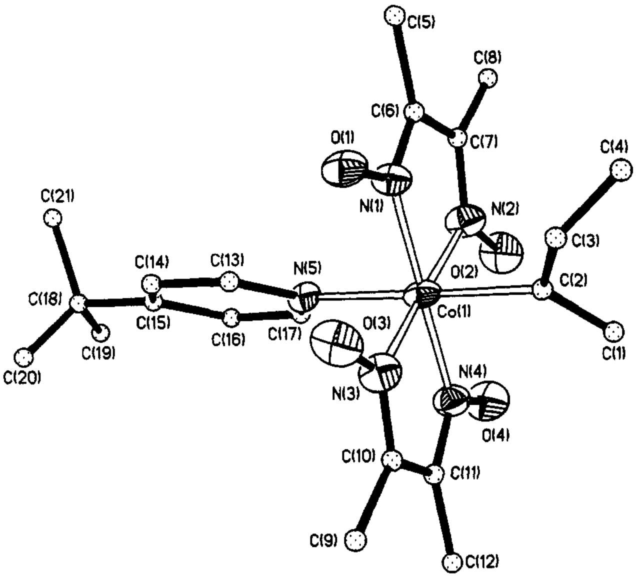
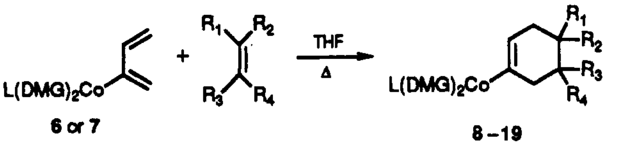


Figure 1.

dienes. The cobalt diene complex **7** has now been characterized by X-ray diffraction,[10] and the C(1)–C(2)–C(3)–C(4) torsion angle is 54.5° (Figure 1). This angle is quite large when compared to reported torsion angles for *s-cis* dienes (5–30°)[11] and torsion angles between the vinyl group and pyrrole ring in X-ray structures of chlorophyll analogues (14–31°).[12] The unusual twist angle for the diene may arise from steric origins manifested in a displacement of C(1) resulting from very short intramolecular interactions with O(4) and N(4). The H(1α) contact distances of 2.46 and 2.44 Å to O(4) and N(4), respectively, are in a range normally associated with hydrogen bonding. The diene distortion may be further accentuated by intermolecular contacts of the pyridyl *tert*-butyl groups, which pack head to tail with the diene; e.g., the H(3)···C(20) distance is 2.92 Å. The C=C bond lengths in **7** are within experimental error of a normal C=C bond length (1.337(6) Å),[13] and the cobalt–carbon bond (1.954(15) Å) is not particularly short when compared to cobalt–carbon bonds in related complexes (1.93–2.09 Å).[8,9,14]

Table II. Diels–Alder Reactions of Cobalt Complexes 6 and 7



entry no.	diene	dienophile	yield, %	regiochem (para:meta)	product
1	**6**	diethyl acetylenedicarboxylate	72		**8**
2	**6**	maleic anhydride	80		**9**
3	**6**	benzoquinone	99		**10**
4	**6**	dimethyl fumarate	62		**11**
5	**6**	dimethyl maleate	34		**12**
6	**6**	dimethyl methylenemalonate	96	>20:1 para	**13**
7	**6**	diethyl methylenemalonate	96	>20:1 para	**14**
8	**7**	diethyl methylenemalonate	69	>20:1 para	**15**
9	**6**	methyl methacrylate	69	9.2:1	**16**
10	**6**	ethyl methacrylate	63	7.9:1	**17**
11	**6**	methyl acrylate	70	5.0:1	**18**
12	**6**	ethyl acrylate	85	5.0:1	**19**

We reasoned that if **6** and **7** exist predominantly in conformations close to *s-cis* in solution, then one would expect them to participate in Diels–Alder reactions under very mild conditions.[15,16] We were gratified to discover that the cobalt diene complexes **6** and **7** react with a variety of dienophiles to produce air-stable cobalt-substituted cyclohexenes in good yield (Table II). All cycloadditions were carried out in refluxing tetrahydrofuran with a slight excess of the dienophile present (maleic anhydride and

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(10) Crystallographic data for $C_{21}H_{32}CoN_5O_4$: M_r = 477.4, monoclinic, $P2_1/c$, a = 9.376(4) Å, b = 22.260(9) Å, c = 11.485(4) Å, V = 2388.2(18) Å^3, Z = 4, D_{calcd} = 1.328 g cm^{-3}, μ(Mo Kα) = 7.49 cm^{-1}, Mo Kα radiation (λ = 0.710 73 Å) with graphite monochromator, T = 298 K, $R(F)$ = 8.08%, $R(wF)$ = 8.10%. Intensities were collected on a Siemens P4 diffractometer using ω-scan methods (4° ≤ 2θ ≤ 45°). Of 3304 data collected, 3123 were unique, and 1428 were independent and observed with $F_o \geq 4.0\sigma(F_o)$. No absorption correction was applied (low μ). The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares methods (G. Sheldrick, Siemens XRD, Madison, WI). All non-hydrogen atoms, except carbon, were refined anisotropically. The three terminal methyl groups of the *tert*-butyl group are disordered in two locations with occupancies of 0.65 and 0.35.

(11) For some examples see: (a) Brouwer, A. M.; Bezemer, L.; Jacobs, H. J. C. *Recl. Trav. Chim. Pays-Bas* **1992**, *111*, 138. (b) Saltiel, J.; Sears, D. F.; Sun, Y.-P.; Choi, J.-O. *J. Am. Chem. Soc.* **1992**, *114*, 3607. (c) Brouwer, A. M.; Conrelisse, J.; Jacobs, H. J. C. *Tetrahedron* **1987**, *43*, 435. (d) Squillacote, M. E.; Sheridan, R. S.; Chapman, O. L.; Anet, F. A. L. *J. Am. Chem. Soc.* **1979**, *101*, 3657. (e) Devaquet, A. J. P.; Townshend, R. E.; Hehre, W. J. *J. Am. Chem. Soc.* **1976**, *98*, 4068.

(12) (a) Fischer, M. S.; Templeton, D. H.; Zalkin, A.; Calvin, M. *J. Am. Chem. Soc.* **1972**, *94*, 3613. (b) Serlin, R.; Chow, H.-C.; Strouse, C. E. *J. Am. Chem. Soc.* **1975**, *97*, 7230, 7237.

(13) Mitchell, A. D., Cross, L. C., Ed. *Tables of Interatomic Distances and Angles*; The Chemical Society: London, 1958.

(14) (a) Randaccio, L.; Bresciani-Pahor, N.; Toscano, P. J.; Marzilli, L. G. *J. Am. Chem. Soc.* **1981**, *103*, 6347. (b) Randaccio, L.; Bresciani-Pahor, N.; Toscano, P. J.; Marzilli, L. G. *Inorg. Chem.* **1981**, *20*, 2722. (c) Randaccio, L.; Bresciani-Pahor, N.; Toscano, P. J.; Marzilli, L. G. *J. Am. Chem. Soc.* **1980**, *102*, 7373. (d) Marzilli, L. G.; Toscano, P. J.; Randaccio, L.; Bresciani-Pahor, N.; Calligaris, M. *J. Am. Chem. Soc.* **1979**, *101*, 6754. (e) Bigotto, A.; Zangrando, E.; Randaccio, L. *J. Chem. Soc., Dalton Trans.* **1976**, 96. (f) Calligaris, M.; Nardin, G.; Randaccio, L. *J. Chem. Soc., Dalton Trans.* **1972**, 1433.

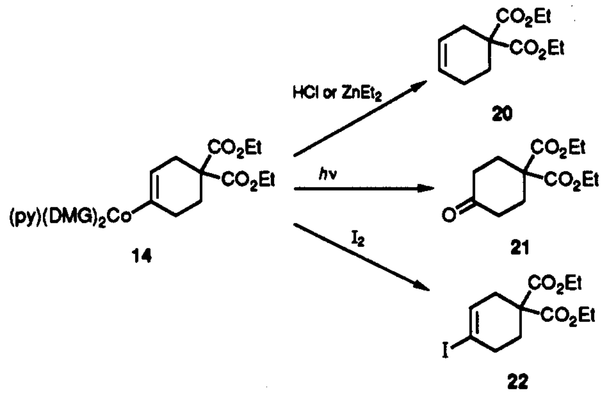
(15) Fringuelli, F.; Taticchi, A. *Dienes in the Diels–Alder Reaction*; Wiley: New York, 1990; Chapter 1.

(16) For some other examples of stoichiometric reactions of transition-metal complexes in Diels–Alder reactions see: (a) Anderson, B. A.; Wulff, W. D.; Powers, T. S.; Tribbitt, S.; Rheingold, A. L. *J. Am. Chem. Soc.* **1992**, *114*, 10784. (b) Bhaduri, D.; Nelson, J. H.; Day, C. L.; Jacobson, R. A.; Solujic, L.; Milosavljevic, E. B. *Organometallics* **1992**, *11*, 4069. (c) Park, J.; Kang, S.; Whang, D.; Kim, K. *Organometallics* **1992**, *11*, 1738. (d) Park, J.; Kang, S.; Whang, D.; Kim, K. *Organometallics* **1991**, *10*, 3413. (e) Ji, H.-L.; Nelson, J. H.; De Cian, A.; Fischer, J.; Solujic, L.; Milosavljevic, E. B. *Organometallics* **1992**, *11*, 1840. (f) Bao, J.; Dragisich, V.; Wenglowsky, S.; Wulff, W. D. *J. Am. Chem. Soc.* **1991**, *113*, 9873. (g) Donaldson, W. A.; Tao, C.; Bennett, D. W.; Grubisha, D. S. *J. Org. Chem.* **1991**, *56*, 4563. (h) Benvegnu, T.; Martelli, J.; Gree, R.; Toupet, L. *Tetrahedron Lett.* **1990**, *31*, 3145. (i) Herndon, J. W. *J. Am. Chem. Soc.* **1987**, *109*, 3165. (j) Herndon, J. W. *J. Org. Chem.* **1986**, *51*, 2853. (k) Lenhert, P. G.; Lukehart, C. M.; Sachsteder, L. *J. Am. Chem. Soc.* **1986**, *108*, 793. (l) Davies, S. G.; Walker, J. C. *J. Chem. Soc., Chem. Commun.* **1986**, 609.

diethyl methylenemalonate will react with **6** without heating). All the symmetrical dienophiles reacted to produce a single adduct. The reactions of dimethyl fumarate and dimethyl maleate provided us with the first indications of how the steric bulk of the complex may influence the outcome of Diels–Alder reactions. The reaction was markedly slower with dimethyl fumarate than with the cyclic dienophiles, and dimethyl maleate produced only a 34% yield of cycloadduct (the balance was unreacted diene **6**) after 64 h at reflux. Reaction of the dienophiles with **6** through an endo transition state will place one of the dienophile substituents on noncyclic *cis* dienophiles in close proximity to the metal and its ligand set. The rate of Diels–Alder reactions in those cases would be expected to slow significantly.

Reactions of **6** and **7** with unsymmetrical dienophiles (Table II, entires 6–12) produced mainly para products in reasonable isolated yields with good to excellent regioselectivity. These regiochemical results compare quite favorably with those of other thermal Diels–Alder reactions for dienes substituted with electron-donating groups in the 2-position.[17] The effect of cobalt substitution in the diene on the rates of these Diels–Alder reactions is much more dramatic. The cobalt-substituted butadiene **6** reacted with diethyl methylenemalonate almost 50 times faster than 2-(trimethylsiloxy)butadiene.[18] The iron complex **5** had previously shown similarly enhanced reactivity with dimethyl acetylenedicarboxylate.[1d] The cobalt complex **6** reacted with diethyl methylenemalonate in THF under pseudo-first-order conditions with a rate constant of 1.25×10^{-3} L mol^{-1} s^{-1} ($t_{1/2}$ = 9.2 min) at 24 °C. In contrast, 2-(trimethylsiloxy)butadiene reacted with this dienophile under identical conditions with a rate constant of 2.54×10^{-5} L mol^{-1} s^{-1} and isoprene showed no evidence of reaction when heated for 2 h in a sealed tube at 80 °C with this dienophile in THF. Whether this dramatic effect on cycloaddition rates by this low-valent, electron-rich cobalt substitution is primarily due to steric or electronic effects will be probed in the future.

With conditions for effecting cycloadditions well worked out, we next turned our attention to the development of methods for cleavage of the cobalt–carbon bonds in the cycloadducts which would yield organic products as well as a cobalt complex which could be recycled into the synthesis of the starting diene complex (**6** or **7**). When cobalt complex **14** was treated with aqueous HCl,[19] we isolated 4,4-dicarboethoxycyclohexene (**20**) (38%) and 4,4-dicarboethoxycyclohexanone (**21**) (42%). Anhydrous HCl produces alkene **20** (75%) with a small amount of ketone **21** (10%). Acidic hydrogen peroxide produces ketone **21** (48%) along with a trace of alkene **20** (2%). Photolysis of **14** in CH_2Cl_2 in the presence of oxygen produced ketone **21** in even better yield (61%). Whether these cleavage products arise via cationic cobalt carbene complex intermediates or cobalt peroxo species[20] will be explored in the future. Oxidative cleavage with iodine yields vinyl iodide **22** (79%), whereas reductive cleavage using diethylzinc also produces alkene **20** (83%). Cobalt recovery is also exceptionally easy in all cases. The crude products from the HCl and photolysis reactions are triturated with diethyl ether to remove the organic cleavage product **20** or **21**. The green water-soluble residue which we believe is the pyridinium salt of $(DMG)_2CoCl_2$[21] is simply dissolved in methanol and treated with pyridine to produce (py)$(DMG)_2CoCl$[6] (89% from the HCl cleavage, 69% from the photolysis), from which the cobalt anion **1b** used to synthesize diene complex **6** can be regenerated.[22] The iodine cleavage yields (py)$(DMG)_2CoI$[23] (92%) after trituration to remove **22**, and the diethylzinc cleavage yields (py)$(DMG)_2CoEt$[6] (88%) after trituration to remove **20**. This cobalt recovery will become particularly important when we use optically active glyoxime ligands[24] in these Diels–Alder reactions.



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Supplementary Material Available: Text giving experimental details and spectroscopic and analytical data for all new compounds and tables of crystal data and data collection and structure solution parameters, thermal parameters, positional parameters, bond distances, and bond angles for **7** (18 pages). Ordering information is given on any current masthead page.

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[17] For reviews of the regio- and stereochemistry of Diels–Alder reactions see: (a) Titov, Y. A. *Russ. Chem. Rev. (Engl.Transl.)* **1962**, *31*, 267. (b) Martin, J. G.; Hill, R. K. *Chem. Rev.* **1961**, *61*, 537. (c) Sauer, J. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 211.

[18] Jung, M. E.; McCombs, C. A. *Tetrahedron Lett.* **1976**, 2935.

[19] (a) Baker, R.; Exon, C. M.; Rao, V. B.; Turner, R. W. *J. Chem. Soc., Perkin Trans. 1* **1982**, 295. (b) Abram, T. S.; Baker, R.; Exon, C. M.; Rao, V. B.; Turner, R. W. *J. Chem. Soc., Perkin Trans. 1* **1982**, 301 and references therein.

[20] Branchaud, B. P.; Meier, M. S.; Malekzadeh, M. N. *J. Org. Chem.* **1987**, *52*, 212 and references therein.

[21] Nakahara, A. *Bull. Chem. Soc. Jpn.* **1955**, *28*, 207.

[22] (a) Schrauzer, G. N.; Deutsch, E. *J. Am. Chem. Soc.* **1969**, *91*, 3341. (b) Schrauzer, G. N.; Kohnle, J. *Chem. Ber.* **1964**, *97*, 3056.

[23] Toscano, P. J.; Seligson, A. L.; Curran, M. T.; Skrobutt, A. T.; Sonnenberger, D. C. *Inorg. Chem.* **1989**, *28*, 166.

[24] (a) Nakamura, A.; Konishi, A.; Tatsuno, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 3443. (b) Nakamura, A.; Konishi, A.; Tsujitani, R.; Kodo, M.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 3449.