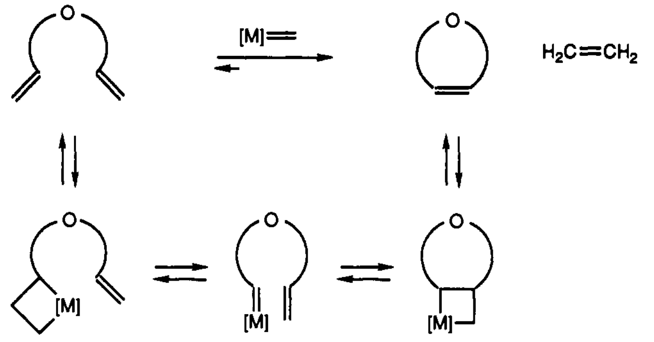
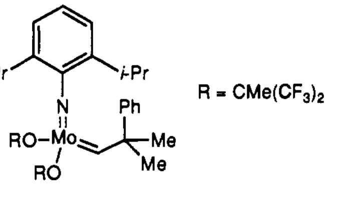
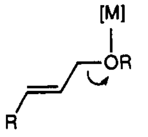
Scheme I



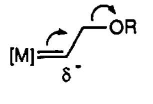


1

Initially, the potential incompatibility of an allylic ether with the metathesis reaction conditions represented a cause for concern. Decomposition of this functionality, as well as the catalyst, has been observed in some olefin metathesis systems, possibly due to Lewis acid activation by the metal (**2**) or to elimination from an alkylidene intermediate (**3**).[11] However, we found that treatment of a diallyl ether with 5 mol % of catalyst **1** at 20 °C affords the desired 2,5-dihydrofuran without complication (Table I, entry 1). The absence of decomposition may be attributable to the relatively low Lewis acidity of **1**, as well as to the short lifetime of **3** due to rapid intramolecular trapping by the tethered olefin.



2



3

The examples provided in Table I illustrate the scope of the catalytic ring-closing metathesis reaction.[12,13] All three olefin substitution patterns have been generated in the case of the 2,5-dihydrofurans (entries 1–3). It is worth noting that formation of the trisubstituted (entry 2) and tetrasubstituted (entry 3) alkenes requires the metathesis of an acyclic *tri*substituted olefin, a process which has not been observed *inter*molecularly with **1**.[9] Catalytic ring-closing metathesis also affords efficient access to dihydropyrans (entries 4 and 5). Entries 6–8 illustrate the synthesis of seven-membered heterocycles and demonstrate the tolerance of the cyclization process to potentially sensitive acetal (entry 7) and silylene (entry 8) functionalities.

Thus, catalytic ring-closing olefin metathesis of diene–ethers provides access to an array of unsaturated oxygen heterocycles from readily available precursors. The application of ring-closing metathesis to the generation of a variety of other cyclic structures, as well as to the stereoselective synthesis of olefins, is currently under investigation.

Acknowledgment. Support has been provided by the National Science Foundation (grant to R.H.G. and postdoctoral fellowship to G.C.F.) and the National Institutes of Health.

Registry No. 1, 139220-25-0; 2-butenyl 1-phenyl-2-butenyl ether, 141412-43-3; 2-butenyl 1-phenyl-2-methyl-2-butenyl ether, 141412-44-4; 2-isobutenyl 1-phenyl-2-methyl-2-butenyl ether, 141412-45-5; 2-butenyl 1-phenyl-3-butenyl ether, 141412-46-6; 2-isobutenyl 1-phenyl-3-butenyl ether, 141412-47-7; 2-butenyl 1-phenyl-4-heptenyl ether, 141412-48-8; 1,1-bis(2-butenoxy)-2-phenylethane, 141412-49-9; bis(2-butenoxy)-methylphenylsilane, 141412-50-2; 2,5-dihydro-2-phenylfuran, 124244-39-9; 2,5-dihydro-3-methyl-2-phenylfuran, 56790-81-9; 2,5-dihydro-3,4-dimethyl-2-phenylfuran, 141412-51-3; 3,6-dichloro-2-phenyl-2*H*-pyran, 126087-54-5; 3,6-dihydro-5-methyl-2-phenyl-2*H*-pyran, 141412-52-4; 2-phenyl-2,3,4,7-tetrahydrooxepin, 54159-34-1; 4,7-dihydro-2-phenyl-1,3-dioxepin, 84473-75-6; *cis*-1,4-dihydroxy-2-butene, 6117-80-2.

Supplementary Material Available: Characterization data for all reaction products (4 pages). Ordering information is given on any current masthead page.

---

(10) Catalyst **1** is both air- and moisture-sensitive. It is available from Strem Chemicals, Inc., 7 Mulliken Way, Newburyport, MA.

(11) Levisalles, J.; Rudler, H.; Villemin, D. *J. Organomet. Chem.* **1979**, *164*, 251–257.

(12) Typical experimental procedure (Table I, entry 4): The diene–ether (101 mg, 0.50 mmol) was added to a homogeneous yellow solution of **1** (19 mg, 0.025 mmol) in 13 mL of dry C_6H_6 under argon. The resulting mixture was stirred at 20 °C for 15 min, at which time TLC showed the reaction to be complete. The reaction mixture was quenched by the addition of water, extracted (1 N HCl/Et_2O), dried over $MgSO_4$, filtered, and concentrated. Flash chromatography (0 → 7% EtOAc/hexane) yielded 74 mg (92%) of the dihydropyran, a colorless oil. Note: The presence of impurities in the reaction mixture can result in significant inhibition of the ring-closing metathesis process.

(13) Preliminary experiments indicate that cyclization also proceeds smoothly in CH_2Cl_2, whereas coordinating solvents such as THF appear to be less suitable. The tungsten analogue of **1** (Schrock, R. R.; DePue, R. T.; Feldman, J.; Schaverien, C. J.; Dewan, J. C.; Liu, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 1423–1435) and $W(CHAr')(NAr)[OCMe(CF_3)_2]_2(THF)$ ($Ar' =$ o-$MeOC_6H_4$, $Ar = 2,6$-$(i$-$Pr)_2C_6H_3$) (Johnson, L. K.; Virgil, S. C.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 5384–5385) also catalyze ring closure; however, in cyclizations in which the low molecular weight olefin generated is not 1,2-disubstituted, the formation of relatively stable tungsten metallacycles appears to inhibit metathesis. Attempts to use ill-defined, "classical" metathesis catalysts (e.g., $WCl_6/SnMe_4$) to effect the reaction have thus far been unsuccessful.

Amide Cuprate Reagents as a New Class of Nitrogen Nucleophiles. Application to Asymmetric Synthesis of β-Lactams[†]

Yoshinori Yamamoto,* Naoki Asao, and Tadao Uyehara

Department of Chemistry, Faculty of Science
Tohoku University, Sendai 980, Japan

Received February 10, 1992

Nitrogen anions R_2N^- are commonly used as strong bases for deprotonation of organic compounds. However, nucleophilic reactions of R_2NM, such as conjugate addition to enoates, have received little attention.[1] We report that cuprates $(R_2N)_2CuLi$ and higher order cyano cuprates $(R_2N)_2Cu(CN)Li_2$ are useful for asymmetric 1,4-addition to enoates[2] and that a highly efficient chiral synthesis of β-lactams is realized by the conjugate addition of these reagents followed by trapping with aldehydes (three-component coupling)[3] (eq 1).

Regioselectivities in the reaction of **1** with R^3R^4NM are summarized in Table I. The reaction of **1a** with the copper reagent gave **2** with relatively good 1,4-regioselectivity (entries 1 and 2)

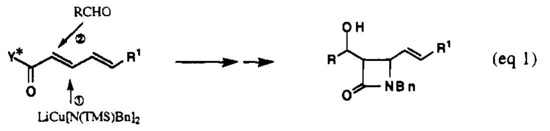
[†] This paper is dedicated to Professor Emeritus Herbert C. Brown on the occasion of his 80th birthday.

(1) Rathke, M. W.; Sullivan, D. *Tetrahedron Lett.* **1972**, 4249. Herrmann, J. L.; Kieczykowski, G. R.; Schlessinger, R. H. *Ibid.* **1973**, 2433. Little, R. D.; Dawson, J. R. *Ibid.* **1980**, *21*, 2609. Hase, T. A. Kukkola, P. *Synth. Commun.* **1980**, *10*, 451.

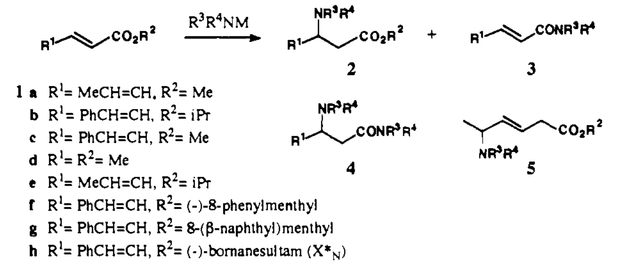
(2) "Higher order" indicates that the stoichiometry of R_2N, Cu, CN, and Li is 2:1:1:2, and it does not mean that the copper species possesses the structure $(R_2N)_2Cu(CN)Li_2$. CuI was used as a source of Cu for $(R_2N)_2CuLi$, and CuCN was used for $(R_2N)_2Cu(CN)Li_2$. For discussions on higher order cyano cuprates, see: Bertz, S. H. *J. Am. Chem. Soc.* **1990**, *112*, 4031. Lipshutz, B. H.; Sharma, S.; Ellsworth, E. L. *Ibid.* **1990**, *112*, 4032.

(3) To our knowledge, a three-component coupling approach to β-lactam synthesis has not been examined although a number of synthetic methods have been reported. For a review, see: (a) Hart, D. J.; Ha, D. C. *Chem. Rev.* **1989**, *89*, 1447. (b) Brynaert, J. M.; Ghosez, L. In *Recent Progress in the Chemical Synthesis of Antibiotics*; Springer-Verlag: Berlin, 1990.

0002-7863/92/1514-5427$03.00/0



(eq 1)



in comparison with the reaction with the lithium reagent (entries 3–5). In entries 1–3 and 6–8, R^3 and R^4 of R^3R^4NM were benzyl and TMS, respectively, with the TMS group being removed during the workup process; R^4 of **2**–**5** was H. With the cuprate analogue **6**, **1b** gave exclusively **2** (entry 6). These results suggested that the copper reagent might be promising for regioselective 1,4-addition to $\alpha,\beta,\gamma,\delta$-dienoates. The selective 1,4-addition to monoenoate **1d** takes place even with the lithium reagent **7** (entry 8).[4] The addition of benzylamine to **1a** produced **5** in 50% yield; no **2**, **3**, or **4** was detected. Accordingly, it is clear that (1) a dienoate gives the δ-adduct with $BnNH_2$, a β-adduct with the copper reagent **6**, and a mixture of **2**–**4** with the lithium reagents and that (2) the presence of an iPr group in R^2 diminishes formation of the 1,2-adduct.

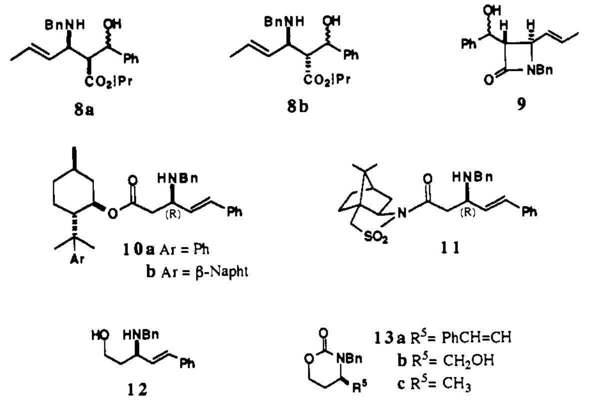
Next we tested whether the three-component coupling was effective with **6**.[5] The conjugate addition of **6** to **1e** followed by trapping with PhCHO gave the desired coupling product **8** in 77% yield. The ratio of **8a**/**8b** was 35:1, although the stereochemistry at COH could not be determined at this stage.[6] Treatment of **8** with KOH/MeOH-H_2O followed by ring closure with PPh_3-$(PyS)_2/CH_3CN$[7] gave **9** (Chart I). Guided by this result, we examined asymmetric synthesis with **6**. The conjugate addition of **6** to **1f** gave **10a** in 80% yield with 72% de, and **1g** produced **10b** in 95% yield with 74% de. The addition to **1h** afforded **11** in 78% yield with 90% de. The diastereomer ratios of **10a**, **10b**, and **11** were determined by their ^1H NMR spectra. The absolute configuration at the β-position of **10a** was determined to be *R* by the following procedure. LAH reduction of **10a** gave **12** in 88% yield. Reaction of **12** with trichloromethyl chloroformate afforded **13a** in 97% yield, which was treated with $O_3/NaBH_4$ to give **13b** in 65% yield. Treatment of **13b** with CBr_4/PPh_3 followed by Bu_3SnH gave **13c** in 30% yield. Comparison of **13c** with authentic material, prepared from (*S*)-3-(benzylamino)butanol,[8] led to the assignment of the *R* configuration (see the supplementary material). The absolute configuration of **11** was determined in a similar manner. It is noteworthy that the *R* configuration is produced in the R^3R^4NM reaction whereas the *S* configuration is obtained in the high-pressure-induced reaction of R^3R^4NH.[9] The "higher order" reagent $[Bn(TMS)N]_2Cu(CN)Li_2$ gave similar results.[10]

Table I. Regioselective 1,4-Addition with Amide Cuprate Reagents[a]

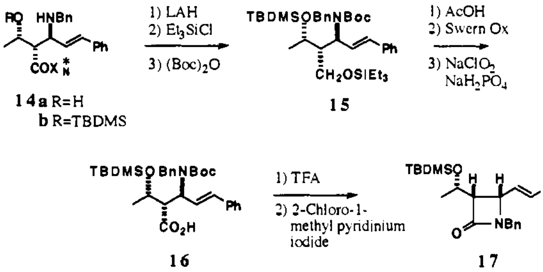
entry	R^3R^4NM	1	isolated yield, % 2	3
1	$[Bn(TMS)N]_2CuLi$ (**6**)	**1a**	54	10
2	Bn(TMS)NLi/cat. CuI	**1a**	60	9
3	Bn(TMS)NLi (**7**)	**1a**	29[b]	18
4	Bn_2NLi	**1a**	*c*	
5	BnNHLi	**1a**		37[b]
6	**6**	**1b**	85	
7	**6**	**1c**	60	10
8	**7**	**1d**	88	

[a] A δ-adduct, which was produced in the direct addition of R^3R^4NH, was not detected in the reaction of R^3R^4NM with **1a–c**. All reactions were carried out at −78 °C. [b] Several unidentified products were formed in addition to major products. [c] The double addition product **4** was obtained in 54% yield.

Chart I



Finally, the three-component coupling was carried out with **1h**. Conjugate addition of the "higher order" reagent to **1h** followed by trapping with acetaldehyde and subsequent protection of the hydroxy group with TBDMSCl gave **14b** in 71% overall yield with 99% de from **1h**. No other diastereomers were detected! Since the free hydroxy form **14a** was unstable, protection was needed prior to isolation and purification. Reduction of **14b** with LAH gave the corresponding alcohol (deprotection of the bornanesultam X^*_N[11]) in 60% yield. Protection of the alcohol with Et_3SiCl and the NH with $(Boc)_2O$ produced **15** in 60% yield. Selective deprotection of the Et_3Si group followed by Swern oxidation and $NaClO_2$ oxidation afforded **16** in 68% yield. Removal of Boc with TFA followed by a standard cyclization procedure[12] gave **17** in 65% yield. Thus, three contiguous chiral centers can be precisely controlled in good yields by the three-component coupling process. Although the absolute stereochemistry of **17** does not correspond to that of natural β-lactams, known technology[3a] can convert it into the correct configuration.



---

[4] Uyehara, T.; Asao, N.; Yamamoto, Y. *J. Chem. Soc., Chem. Commun.* **1987**, 1410; *Ibid.* **1989**, 753. Asao, N.; Uyehara, T.; Yamamoto, Y. *Tetrahedron* **1988**, *44*, 4173; *Ibid.* **1990**, *46*, 4563.

[5] The copper (and/or lithium) enolate, produced in organocuprate conjugate additions, is not suitable for further aldol and alkylation reactions. Normally such an enolate is transmetalated to a zinc or tin enolate. Yamamoto, Y.; Yatagai, H.; Maruyama, K. *Silicon, Germanium, Tin, Lead Compd.* **1986**, *9*, 25. Suzuki, M.; Yanagisawa, A.; Noyori, R. *J. Am. Chem. Soc.* **1985**, *107*, 3348.

[6] The ratio of **8a** to its isomer at COH (**8a′**) was ca. 1:1, and that of **8b** and **8b′** was also ca. 1:1.

[7] Kobayashi, S.; Iimori, T.; Izawa, T.; Ohno, M. *J. Am. Chem. Soc.* **1981**, *103*, 2406.

[8] Estermann, H.; Seebach, D. *Helv. Chim. Acta* **1988**, *71*, 1824.

[9] The high-pressure-induced addition of (1,1-diphenylmethyl)amine to 8-(β-naphthyl)menthyl crotonate produced the (*S*)-β-amino ester (d'Angelo, J.; Maddaluno, J. *J. Am. Chem. Soc.* **1986**, *108*, 8112).

[10] However, the aldehyde trapping reaction proceeds more smoothly and cleanly with the higher order reagent. During our investigation, it was reported that some chiral lithium amides underwent conjugate addition to enoates with high de (Davies, S. G.; Ichihara, O. *Tetrahedron: Asymmetry* **1991**, *2*, 183). We carried out aldehyde trapping with these reagents, but a mixture of several products was obtained.

[11] Oppolzer, W.; Blagg, J.; Rodriguez, I.; Walther, E. *J. Am. Chem. Soc.* **1990**, *112*, 2767.

[12] Huang, H.; Iwasawa, N.; Mukaiyama, T. *Chem. Lett.* **1984**, 1465.

Supplementary Material Available: Listings of experimental procedures for the syntheses of β-lactams, their spectral data, and structure determinations (15 pages). Ordering information is given on any current masthead page.

Novel Arylation of Molecular Nitrogen via Bimetallic Activation: Reaction of Coordinated Dinitrogen with Coordinated Haloarene[1]

Youichi Ishii, Yukiatsu Ishino, Takanori Aoki, and Masanobu Hidai*

Department of Synthetic Chemistry
Faculty of Engineering, The University of Tokyo
Hongo, Bunkyo-ku, Tokyo 113, Japan

Received February 24, 1992

C–N bond formation at coordinated dinitrogen has been attracting much attention in connection with direct synthesis of organo–nitrogen compounds from molecular nitrogen.[2] Of particular interest is the arylation of coordinated dinitrogen from both fundamental and industrial points of view. However, such reactions have rarely been reported in the literature. The only report dealing with the direct arylation of coordinated dinitrogen concerns the reaction of a molybdenum dinitrogen complex having a tetrathia macrocycle ligand with iodo- or bromoarenes to give aryldiazenido complexes.[3] More readily available molybdenum or tungsten dinitrogen complexes having phosphine ligands of the type $M(N_2)_2(L)_4$ (M = Mo or W; L = phosphine) have not been reported to undergo direct arylation.[4] In order to develop a novel method for arylation of coordinated dinitrogen, we have investigated reactions via bimetallic activation, i.e., reactions of coordinated dinitrogen with coordinated haloarenes. Coordination of haloarenes to transition metal complexes is known to be activated toward nucleophilic reactions.[5] Here we report that the bimetallic approach yields μ-aryldiazenido complexes.

Although an attempted reaction of $[W(N_2)_2(dpe)_2]$ (**1**, dpe = $Ph_2PCH_2CH_2PPh_2$) with $[Cr(p\text{-}FC_6H_4COOMe)(CO)_3]$ (**2**) failed to proceed, an anionic dinitrogen complex[6] $[^nBu_4N][W(NCS)(N_2)(dpe)_2]$ (**3a**) smoothly reacted with **2** in THF at room temperature to give a new complex which shows lower ν_{CO} (1948, 1867, 1857 cm^{-1} (KBr)) than those of **2** (1991, 1902 cm^{-1}). The high reactivity of **3a** is attributable to strong back-donation from the anionic tungsten center to coordinated dinitrogen, which is reflected in the low ν_{NN} of **3a** (1860 cm^{-1}). Activation of the haloarene by the $Cr(CO)_3$ moiety must be essential for the reaction, since **3a** failed to react with noncoordinated $p\text{-}FC_6H_4COOMe$.

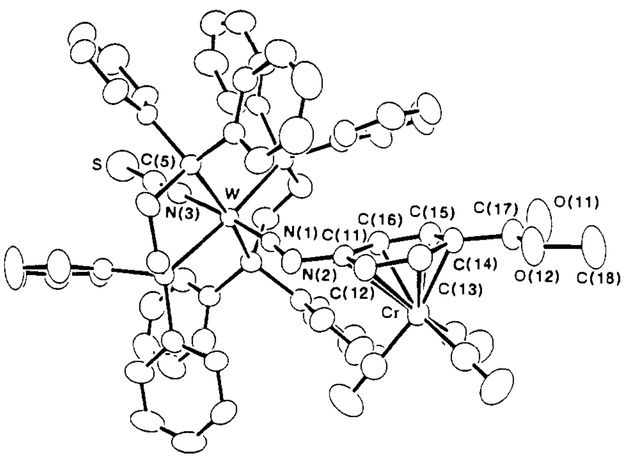
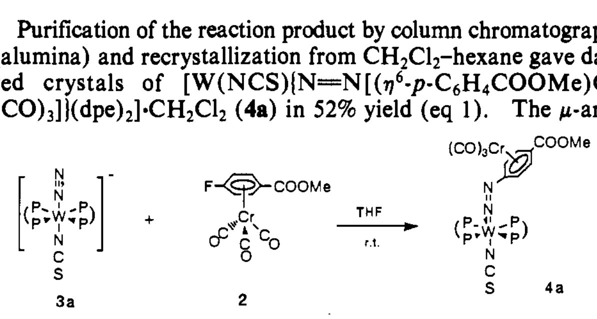
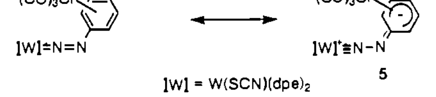


Figure 1. ORTEP view of the structure $[W(NCS)\{N{=}N[(\eta^6\text{-}p\text{-}C_6H_4COOMe)Cr(CO)_3]\}(dpe)_2]$ (hydrogen atoms omitted). Selected bond lengths (Å) and angles (deg): W–N(1), 1.784 (4); N(1)–N(2), 1.314 (5); N(2)–C(11), 1.366 (6); Cr–C(11), 2.431 (5); Cr–C(12), 2.259 (5); Cr–C(13), 2.193 (5); Cr–C(14), 2.174 (5); Cr–C(15), 2.194 (5); Cr–C(16), 2.301 (5); W–N(1)–N(2), 164.9 (3); N(1)–N(2)–C(11), 120.0 (4).

Purification of the reaction product by column chromatography (alumina) and recrystallization from CH_2Cl_2–hexane gave dark red crystals of $[W(NCS)\{N{=}N[(\eta^6\text{-}p\text{-}C_6H_4COOMe)Cr(CO)_3]\}(dpe)_2]\cdot CH_2Cl_2$ (**4a**) in 52% yield (eq 1). The μ-aryldiazenido structure is in good agreement with the above IR data as well as high-field shifted signals of the aromatic hydrogens in the $C_6H_4COOMeCr(CO)_3$ moiety in the ^1H NMR spectrum (δ (C_6D_6) 5.73, d, *J* = 7.3 Hz; 4.11, d, *J* = 7.3 Hz) and is further confirmed by an X-ray diffraction study.[7] As shown in Figure 1, **4a** has a significantly longer N=N bond (1.314 (5) Å) in comparison with similar singly bent diazenido complexes[4,8] (1.16–1.29 Å). It is more in the range of N–N bond lengths of hydrazido[8a,b,9] and diazoalkane[10] complexes (1.25–1.38 Å). Further, the Cr–C(11) bond (2.431 (5) Å) is longer than other Cr–arene carbon bonds (2.174 (5)–2.301 (5) Å). These data indicate the large contribution of resonance structure **5** (eq 2), whose zwitterionic structure is stabilized by the electron-withdrawing $Cr(CO)_3$.



(1)



(2)

---

[1] Preparation and Properties of Molybdenum and Tungsten Dinitrogen Complexes. 37. Part 36: Aoshima, T.; Tanase, T.; Mizobe, Y.; Yamamoto, Y.; Hidai, M. *J. Chem. Soc., Chem. Commun.* **1992**, 586.

[2] (a) Hidai, M.; Mizobe, Y. In *Reactions of Coordinated Ligands*; Braterman, P. S., Ed.; Plenum Press: London, 1988; Vol. 2, p 53. (b) Hidai, M. In *Molybdenum Enzymes*; Spiro, S., Ed.; John Wiley: New York, 1985; p 285. (c) George, T. A. In *Homogeneous Catalysis with Metal Phosphine Complexes*; Pignolet, L. H., Ed.; Plenum Press: New York, 1983; Chapter 13. (d) Dilworth, J. R.; Richards, R. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Eds.; Pergamon Press: Oxford, 1982; Vol. 8, Chapter 60.

[3] Yoshida, T.; Adachi, T.; Ueda, T.; Kaminaka, M.; Sasaki, N.; Higuchi, T.; Aoshima, T.; Mega, I.; Mizobe, Y.; Hidai, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1040.

[4] Chatt, J.; Head, R. A.; Leigh, G. J.; Pickett, C. J. *J. Chem. Soc., Dalton Trans.* **1978**, 1638.

[5] Watts, W. E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Eds.; Pergamon Press: Oxford, 1982; Vol. 8, Chapter 59.

[6] Although **3a** has been referred to as a thiocyanato in literature, its ν_{NCS} (2080 cm^{-1}) as well as the molecular structure of **4a** clearly indicates that it is an isothiocyanato: Chatt, J.; Leigh, G. J.; Neukomm, H.; Pickett, C. J.; Stanley, D. R. *J. Chem. Soc., Dalton Trans.* **1980**, 121.

[7] Crystal data: $M = 1422.89$; monoclinic, space group $P2_1/n$; $a = 24.135$ (3) Å, $b = 20.967$ (5) Å, $c = 12.273$ (5) Å, $\beta = 90.06$ (4)°; $V = 6210$ (5) Å^3; $Z = 4$; $D_{calcd} = 1.522$ g/cm^3, $D_{obsd} = 1.52$ g/cm^3; μ(Mo Kα) = 23.31 cm^{-1}; $R = 0.034$, $R_w = 0.029$ for 7578 reflections with $I > 3.00\sigma(I)$.

[8] (a) Street, A. C.; Mizobe, Y.; Goto, F.; Mega, I.; Oshita, H.; Hidai, M. *Chem. Lett.* **1991**, 383. (b) Hidai, M.; Komori, K.; Kodama, T.; Jin, D.; Takahashi, T.; Sugiura, S.; Uchida, Y.; Mizobe, Y. *J. Organomet. Chem.* **1984**, *272*, 155. (c) Colquhoun, H. M.; Crease, A. E.; Taylor, S. A. *J. Chem. Soc., Chem. Commun.* **1980**, 879. (d) Day, C. S.; Day, V. W.; George, T. A.; Tavanaiepour, I. *Inorg. Chim. Acta* **1980**, *45*, L54. (e) Sato, M.; Kodama, T.; Hidai, M.; Uchida, Y. *J. Organomet. Chem.* **1978**, *152*, 239.

[9] (a) Oshita, H.; Mizobe, Y.; Hidai, M. *Chem. Lett.* **1990**, 1303. (b) Barclay, J. E.; Hills, A.; Hughes, D. L.; Leigh, G. J.; Macdonald, C. J.; Baker, M. A.; Mohd.-Ali, H. *J. Chem. Soc., Dalton Trans.* **1990**, 2503. (c) Hidai, M.; Aramaki, S.; Yoshida, K.; Kodama, T.; Takahashi, T.; Uchida, Y.; Mizobe, Y. *J. Am. Chem. Soc.* **1986**, *108*, 1562. (d) Nishihara, H.; Mori, T.; Tsurita, Y.; Nakano, K.; Saito, T.; Sasaki, Y. *J. Am. Chem. Soc.* **1982**, *104*, 4367. (e) Day, V. W.; George, T. A.; Iske, S. D. A.; Wagner, S. D. *J. Organomet. Chem.* **1976**, *112*, C55.

0002-7863/92/1514-5429$03.00/0