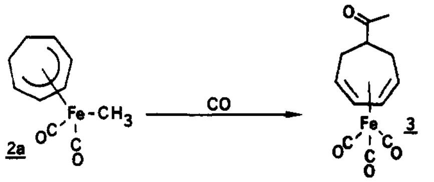
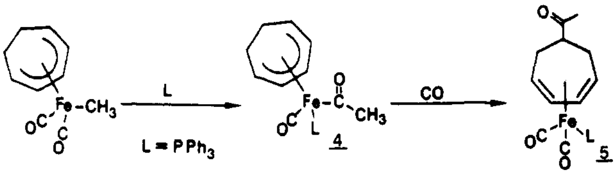
carbons. Other bond lengths and angles are as expected. The angle between the least-squares planes containing C1–C5 and C1, C5, C6, and C7 is 47.1°.[6] The iron–methyl bond length is 2.113 Å. All other data support the suggested structure.[7]

Characterization of **2a** rests on spectroscopic data. At −70 °C, each of the five dienyl protons appears as a distinct multiplet in the ^1H NMR (δ 5.14, 4.42, 4.13, 3.85, 3.25). Upon warming, the multiplets at δ 4.42 and 4.13 (H2,4) merge to a doublet of doublets (δ 4.42). Coalescence of H1 and H5 (δ 3.86, 3.25) occurs at −4 °C (δ 3.71; $\Delta G^{\ddagger} = 13.1$ kcal mol^{-1}).[8] These data are consistent with a rotation of the cycloheptadienyl ligand.[9] At the low-temperature limit, the methyl group must be situated beneath the pentadienyl fragment (approximately aligned with C2 as is found for **2b**). The NMR data can be explained by rotation through either of two possible C_{2v} isomers; however, we can conclude that neither of these conformers reaches an appreciable population since the central pentadienyl proton, as well as the methyl group, remain well resolved at temperatures from 25 °C to −70 °C.

As a first step in contrasting the chemistry of η^5-dienyl metal complexes and their Cp counterparts, we have examined the insertion reactions of **2a** with CO and PPh_3. Solutions of **2a** react with CO (1 atm, THF, 25 °C, 48 h) to give the endo-acylated iron diene complex **3** in 60% yield (eq 2). Presumably CO insertion to give an (η^1-acyl)iron intermediate precedes reductive migration to the bottom face of the η^5-dienyl ligand. Subsequent isomerization and coordination of CO gives **3**. This reaction supports our suggested mechanism for the formation of **3** from a dienyliron anion and acetyl chloride.[10] Although we have no direct evidence for the (η^1-acyl)iron intermediate, treatment of **2a** with excess PPh_3 (THF-d_8, 25 °C, 30 min) provides a new species whose ^1H NMR spectrum is consistent with the η^1-acyl **4** (eq 3).[7,11] This compound exhibits five multiplets for the pentadienyl fragment, one of which is strongly coupled to phosphorus (12.0 Hz); the coupling pattern is similar to that of **2b**. The η^1-acetyl group appears as a singlet at δ 2.31. When generated in situ from solutions of **2a**, **4** reacts with CO to provide the endo-substituted iron diene complex **5** (THF, 48 h, 1 atm of CO, 85%).[7]



(2)



(3)

The CO insertion reactions of **2a** occur much more readily than do those of their isoelectronic counterpart $CpFe(CO)_2CH_3$.[12] The latter require elevated temperature and/or pressure. We attribute this significant difference in reactivity to a facile η^5–η^3 ring slip in the dienyl system; insertion will be promoted by creation of a vacant site for the incoming ligand.[13] Similar η^5–η^3 slippage is known for Cp complexes;[14] however, this process is not common since the aromatic character of the Cp ligand is lost (or at least diminished) in the η^3 form.

Reactivity studies of pentadienyl complexes are currently limited to a few accounts of η^5–η^3 ligand slip induced by neutral donor ligands. The insertion reactions of **2a** suggest that fundamental organometallic reactions requiring a vacant coordination site will occur more readily for η^5-pentadienyl complexes than for their Cp counterparts. Further studies on the reactivity patterns of these and other pentadienyl complexes are in progress.

Acknowledgment. Supported by an Atlantic Richfield Foundation Grant of the Research Corp. We thank Professor Robert J. Doedens and Dr. Tim Hanusa for assistance with the crystal structure.

Supplementary Material Available: Tables of crystallographic data, interatomic distances, bond angles, positional parameters, and temperature factors for **2b** as well as tables of spectroscopic data for **2a**, **2b**, **4**, and **5** (10 pages). Ordering information is given on any current masthead page.

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(6) Kane-Maguire, L. A. P.; Honig, E. D.; Sweigart, D. A. *J. Chem. Soc., Chem. Commun.* **1984**, 345.

(7) Microanalytical data or high-resolution MS, NMR (^1H, ^{13}C, ^{31}P) and IR for new compounds are given in the supplementary material.

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(9) Whitesides, T. H.; Budnik, R. A. *Inorg. Chem.* **1975**, *3*, 664. Knox, S. A. R.; Phillips, R. P.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1976**, 552.

(10) Williams, G. M.; Rudisill, D. E. *J. Am. Chem. Soc.* **1985**, *107*, 3357.

(11) Mixtures of **2a** and **4** are produced by added phosphine. For example, 4 equiv of Ph_3P gives $4/2a \approx 2$. A large excess of PPh_3 is required for complete formation of **4**. We have not isolated analytically pure samples of **4**; this species is very unstable in the absence of excess ligand.

(12) Forschner, T. C.; Cutler, A. R. *Organometallics* **1985**, *4*, 1247. In this paper, and in others,[15] η^5–η^3 ring slip is suggested to account for enhanced rates of insertion for η^5-indenyl complexes.

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Preparation of Molybdenum Pentacarbonyl Complexes of the Ph_2PNSO and $Ph_2PNSNPPh_2$ Ligands: X-ray Crystal Structure and Fluxional Behavior of $(CO)_5MoP(Ph)_2NSN(Ph)_2PMo(CO)_5$

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Summary: The reactions of $(CO)_5Mo(Ph_2PCl)$ with KNSO or K_2SN_2 in acetonitrile produce $(CO)_5Mo(Ph_2PNSO)$ (**3a**) or $(CO)_5MoP(Ph)_2NSN(Ph)_2PMo(CO)_5$ (**4a**), respectively. An X-ray crystal structure determination of **4a** shows that the $Ph_2PNSNPPh_2$ ligand adopts a cis,trans conformation. A variable-temperature ^{31}P NMR spectroscopic study of **4a** provides evidence for a cis,trans → trans,cis interconversion ($\Delta G^{\ddagger}_{213} = 9.4 \pm 0.2$ kcal mol^{-1}) in solution.

Thionylamino derivatives of type **1** are unknown and the only example of a sulfur diimide of type **2** (R = *t*-Bu) was reported by Herberhold et al. in 1984.[1] Other derivatives of **2** (R = Et, Cy, Ph) could not be isolated.[2]

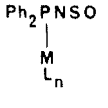
R_2PNSO

1

$R_2PNSNPR_2$

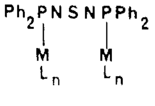
2

The reaction of **2** (R = *t*-Bu) with $Cr(CO)_4(C_7H_8)$ gave an adduct $Cr(CO)_4(C_7H_8)(t\text{-}Bu_2PNSNPBu_2\text{-}t)$ of unknown structure,[2] but no thermally stable metal complexes of the intact ligand **2** have been characterized.[3-6] This report describes the preparation of **3a** and **4a** (ML_n = $Mo(CO)_5$), the facile transformation of **3a** to **4a**, and the X-ray crystal structure and a variable-temperature ^{31}P NMR spectroscopic study of **4a**.



$$\underset{\underset{L_n}{|}}{\overset{}{Ph_2\underset{\substack{|\\M\\L_n}}{P}NSO}}$$

3



$$Ph_2\underset{\substack{|\\M\\L_n}}{P}NSN\underset{\substack{|\\M\\L_n}}{P}Ph_2$$

4

A solution of $(CO)_5Mo(Ph_2PCl)$[7] (2.9 mmol) in acetonitrile (10 mL) was added dropwise to a suspension of KNSO[8] (3.1 mmol) in acetonitrile (10 mL) at −40 °C. The reaction mixture was stirred at room temperature for 30 min. Solvent was removed in vacuo to give a dark yellow oil which was recrystallized from *n*-pentane at −20 °C to give $(CO)_5Mo(Ph_2PNSO)$ (**3a**; 1.4 mmol) as pale orange crystals.[9] If the reaction mixture is allowed to stir at room temperature for 1 day in acetonitrile, there is a ca. 10% conversion of **3a** to the binuclear complex $(CO)_5MoP(Ph)_2NSN(Ph)_2PMo(CO)_5$ (**4a**), but this transformation is not oberved for solutions of recrystallized **3a** in chloroform after 4 h at 50 °C. It is possible that the conversion **3a** → **4a** is catalyzed by basic impurities in the reaction mixture. The complex **3a** is readily hydrolyzed to the known compound $(CO)_5Mo(Ph_2PNH_2)$ in wet solvents.[10]

The complex **4a** is best prepared by the reaction of $(CO)_5Mo(Ph_2PCl)$ with K_2SN_2.[11] A solution of $(CO)_5Mo(Ph_2PCl)$ (1.93 mmol) in acetonitrile (15 mL) was added dropwise (30 min) to a suspension of K_2SN_2 (0.96 mmol) in acetonitrile (15 mL) at −20 °C. The reaction mixture was stirred at room temperature for 17 h. Solvent was removed in vacuo to give an orange oil which was extracted with *n*-pentane. Chromatography on silica gel 60 (230–400 mesh), using *n*-pentane/CH_2Cl_2 (4:1) as eluant, yielded an analytically pure sample of **4a** (0.63 mmol) as dark orange, air-stable crystals.[12]

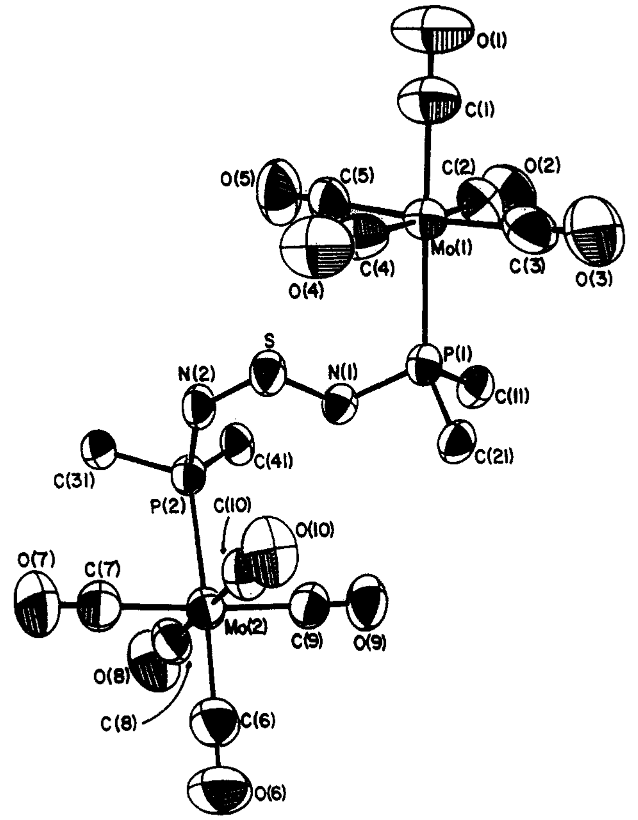


Figure 1. ORTEP plot (50% probability ellipsoids) for $(CO)_5MoP(Ph)_2NSN(Ph)_2PMo(CO)_5$ showing the atomic numbering scheme. For clarity, only the α-carbon atoms of the phenyl rings are included. Selected interatomic distances (Å) and angles (deg): Mo(1)–P(1) = 2.516 (2), Mo(1)–C(1) = 1.983 (7), Mo(1)–C(2) = 2.039 (6), Mo(1)–C(3) = 2.012 (6), Mo(1)–C(4) = 2.022 (5), Mo(1)–C(5) = 2.030 (5), Mo(2)–P(2) = 2.494 (2), Mo(2)–C(6) = 1.997 (6), Mo(2)–C(7) = 2.031 (5), Mo(2)–C(8) = 2.022 (4), Mo(2)–C(9) = 2.035 (5), Mo(2)–C(10) = 2.055 (4), P(1)–N(1) = 1.732 (3), N(1)–S = 1.529 (4), S–N(2) = 1.515 (3), N(2)–P(2) = 1.706 (3), Mo(1)–P(1)–N(1) = 117.2 (1), P(1)–N(1)–S = 117.9 (2), N(1)–S–N(2) = 116.0 (2), S–N(2)–P(2) = 130.8 (2), N(2)–P(2)–Mo(2) = 112.9 (1).

Crystals of **4a** suitable for an X-ray structural analysis were obtained by recrystallization from *n*-pentane.[13] The molecular geometry and atomic numbering scheme are illustrated in Figure 1. The sulfur diimide ligand **2** (R = Ph) adopts a cis,trans conformation with S–N bond lengths

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(1) Herberhold, M.; Ehrenreich, W.; Guldner, K. *Chem. Ber.* **1984**, *117*, 1999.

(2) Ehrenreich, W. P. Ph.D. Diss., Universität Bayreuth, 1983.

(3) The reactions of $t\text{-}Bu_2PNSNPBu_2\text{-}t$ with $H_2Os_3(CO)_{12}$[4] or $CpW(CO)_3H$[5] give complexes in which the ligand is modified by insertion into a metal–hydrogen bond. In the former case, the initial product $H_2Os_3(CO)_{10}(t\text{-}Bu_2PNSNPBu_2\text{-}t)$ decomposes above 0 °C to give $HOs_3(CO)_9[Pt\text{–}Bu_2N(H)S]$.[6]

(4) Ehrenreich, W.; Herberhold, M.; Suss-Fink, G.; Klein, H.-P.; Thewalt, U. *J. Organomet. Chem.* **1983**, *248*, 171.

(5) Herberhold, M.; Ehrenreich, W.; Guldner, K.; Jellen, W.; Thewalt, U.; Klein, H.-P. *Z. Naturforsch, B: Anorg. Chem., Org. Chem.* **1983**, *38B*, 1383.

(6) A monodentate complex of the related ligand $t\text{-}Bu_2PNSNAsBu_2\text{-}t$ with $H_2Os_3(CO)_{12}$, in which the –N═S═N– unit is intact, has been reported very recently. Ehrenreich, W.; Herberhold, M.; Herrmann, G.; Suss-Fink, G.; Gieren, A.; Hubner, T. *J. Organomet. Chem.* **1985**, *294*, 183.

(7) Kraihanzel, C. S.; Bartish, C. M. *J. Am. Chem. Soc.* **1972**, *94*, 3572.

(8) Armitage, D. A.; Brand, J. C. *J. Chem. Soc., Chem. Commun.* **1979**, 1078.

(9) Anal. Calcd for $C_{17}H_{10}MoNO_6PS$: C, 42.25; H, 2.09; N, 2.90. Found: 42.32; H, 2.14; N, 2.92. $^{31}P\{^1H\}$ NMR (in $CDCl_3$): +92.4 (s) ppm (reference 85% H_3PO_4). IR: in *n*-pentane 2074 m, 1961 vs, 1954 vs (terminal CO) cm^{-1}; in Nujol, 1233 s (ν_{as}(NSO)), 1103 m and 1091 m (ν_s(NSO)) cm^{-1}.

(10) The hydrolysis product had the same IR spectrum and ^{31}P NMR chemical shift (+66.7 ppm) as an authentic sample of $(CO)_5Mo(Ph_2PNH_2)$ prepared from $(CO)_5Mo(Ph_2PCl)$ by the literature procedure. Kraihanzel, C. S.; Bartish, C. M. *J. Organomet. Chem.* **1972**, *43*, 343.

(11) Herberhold, M.; Ehrenreich, W. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 633.

(12) Anal. Calcd for $C_{34}H_{20}Mo_2N_2O_{10}P_2S$: C, 45.25; H, 2.23; N, 3.10. Found: C, 45.03; H, 2.10; N, 3.10. $^{31}P\{^1H\}$ NMR (in $CDCl_3$ at 25 °C): +89.6 (s) ppm. IR: in *n*-hexane 2075 m, 1994 s, and 1955 s br (terminal CO) cm^{-1}; in Nujol, 1193 s (ν_{as}(NSN)) and 1092 m (ν_s(NSN) cm^{-1}.

(13) A dark orange crystal (approximate dimensions 0.3 × 0.3 × 0.2 mm^3) mounted in a glass capillary under inert atmosphere. Crystal data: space group $P2_1/c$, a = 11.018 (2) Å, b = 30.275 (4) Å, c = 12.757 (3) Å, β = 115.11 (9)°, V = 3853 (1) $Å^3$, Z = 4, ρ_{calcd} = 1.55 g cm^{-3}, μ(Mo Kα, graphite monochromator) = 8.32 cm^{-1}; $\omega/2\theta$ scan data collection at room temperature ($1.5 < \theta < 25°$); 6756 unique reflections, 3736 observed ($I > 3\sigma(I)$), 5559 observed plus those with $I_c > 3\sigma(I_o)$ used in final cycles); CAD4F diffractometer, structure solved by Patterson and difference Fourier techniques and refinement by block cascading least squares (XRAY76); data corrected for absorption by analytical technique (DIFABS); all non-hydrogen refined anisotropically, H included in calculated positi ons with a temperature factor set to 1.1 × B (equiv) of bonded C atom; R = 0.035, R_w = 0.030, $w = [\sigma^2(F) + 0.0001F^2]^{-1}$, 460 variables, GOF = 1.05, maximum residual electron density = 0.55 e $Å^{-3}$.

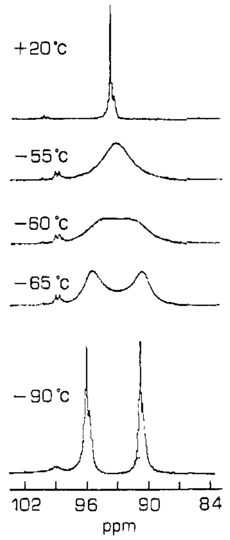
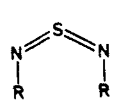


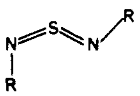
Figure 2. Variable-temperature $^{31}P\{^1H\}$ NMR spectra of $(CO)_5MoP(Ph)_2NSN(Ph)_2PMo(CO)_5$ in acetone-d_6.

of 1.529 (4) and 1.515 (3) Å and P–N bond lengths of 1.732 (3) and 1.706 (3) Å. The longer S–N and P–N bonds are associated with N(1) for which PNS = 117.9 (2)°, cf. P-(2)N(2)S = 130.8 (2)°. The NSN angle is 116.0 (2)°. Thus the overall geometry and detailed structural parameters are very similar to those reported for t-$Bu_2P(X)NSN(X)PBu_2$-t (X = S, Se).[14]

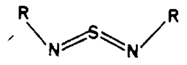
Three geometrical isomers are possible for sulfur diimides: cis,cis (**5a**), cis,trans (**5b**), and trans,trans (**5c**). Ab initio MO calculations for MeNSNMe indicate that **5b** is the lowest energy form and provide a value of 16.0 kcal mol^{-1} for the cis,trans to trans,cis interconversion barrier, which is expected to decrease with increasing bulk of the substituents R.[15] This process is thought to occur via the intermediacy of the cis,cis isomer in view of the substantially higher energy of the trans,trans isomer.[15]



5a



5b



5c

As indicated in Figure 2 the $^{31}P\{^1H\}$ NMR spectrum of **4a** in acetone-d_6 at −90 °C shows two equally intense singlets at +96.0 and +90.5 ppm consistent with the existence of the cis,trans isomer in solution at this temperature.[16] When the temperature of the solution is gradually raised, these two signals broaden and collapse until at +20 °C a single, sharp singlet is observed at +93.7 ppm. The reverse of these changes is observed when the solution is cooled again to −90 °C. These observations are consistent with a rapid cis,trans to trans,cis interconversion. The coalescence temperature is −60 °C, which corresponds to an interconversion barrier of 9.4 ± 0.2 kcal mol^{-1}[17] consistent with the prediction of ab initio MO calculations (vide supra).[15] By contrast, no indication of nonequivalence of the two phosphorus substituents in solution was observed for t-$Bu_2P(X)NSN(X)PBu_2$-t (X = S, Se) at −80 °C in CD_2Cl_2[14] or for **2** (R = t-Bu) at −100 °C in CD_2Cl_2.[18,19]

Heterocumulenes of the type RNSO and RNSNR (R = alkyl, aryl) form a variety of mono- and binuclear complexes with organometallic substrates, which may involve M—N, M—S, or M—π-N═S bonding.[20] The preparation of **3a**, the first metal complex of **1**, provides an opportunity to explore the coordination chemistry of this interesting ligand. The extension of the preparative routes described herein to the synthesis of complexes of $RP(NSO)_2$ and $P(NSO)_3$ (and the corresponding sulfur diimides) is another intriguing prospect, which is being pursued.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for financial support in the form of an operating grant (T.C.) and an infrastructure grant for the X-ray structural service. We also thank Dr. K. A. Kerr for the use of the X-ray diffractometer.

Registry No. **3a**, 100815-28-9; **4a**, 100815-29-0; **5b**, 84878-03-5; $(CO)_5Mo(Ph_2PCl)$, 23581-74-0.

Supplementary Material Available: Listings of positional and thermal parameters, all bond distances and bond angles, and observed and calculated structure factors (32 pages). Ordering information is given on any current masthead page.

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[14] Herberhold, M.; Ehrenreich, W.; Gieren, A.; Betz, H; Hubner, T. *Chem. Ber.* **1985**, *118*, 1476. For example, the corresponding data for t-$Bu_2P(S)NSN(S)PBu_2$-t are d(S–N) = 1.527 (1) and 1.513 (1) Å, d(P–N) = 1.702 (1) and 1.697 (1) Å, PN(1)S = 118.4 (1)°, PN(2)S = 136.4 (1)°, and NSN = 116.9 (1)°.

[15] Raghavachari, K.; Haddon, R. C. *J. Phys. Chem.* **1983**, *87*, 1308.

[16] The alternative explanation of the ^{31}P NMR spectrum is that *equal amounts* of the isomers **5a** and **5c** are present at −90 °C. This is very unlikely in view of the steric repulsions between bulky R groups in **5a** and the high energy calculated for **5c** (R = Me).[15]

[17] Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982.

[18] Herberhold, M.; Ehrenreich, W.; Guldner, K. *Chem. Ber.* **1984**, *117*, 1999.

[19] The structure of **2** (R = Bu-t) in the solid state is unknown, but IR data suggest the existence of two isomers.[2] However, the corresponding arsenic compound has been shown by X-ray crystallography to adopt a cis,cis configuration. Gieren, A.; Betz, H.; Hubner, T.; Lamm, V.; Herberhold, M.; Guldner, K. *Z. Anorg. Allg. Chem.* **1984**, *513*, 160.

[20] Vrieze, K.; van Koten, G. *J. R. Neth. Chem. Soc.* **1980**, *99*, 145.

Reversible Metalation of Alkyl and Aryl Groups by a Coordinatively Unsaturated Iron Complex

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Summary: The coordinatively unsaturated iron(0) species $Fe(DEPE)_2$ [DEPE = 1,2-bis(diethylphosphino)ethane] was generated, and its reactions with C–H bonds in alkyl groups and arenes were investigated.

Recently, a number of workers have reported the reaction of alkyl C–H bonds with complexed transition metals including iridium,[1] rhodium,[2] rhenium,[3] and tungsten.[4] In each of the reported cases, the reactive metal species has been coordinatively unsaturated (formally electron deficient) and hence potentially electrophilic. In the absence of better sources of electrons, an accessible C–H bond can

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[1] Hoyano, J. K.; McMaster, A. D.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 7190–1. Bergman, R. G.; Janowicz, A. H. *J. Am. Chem. Soc.* **1982**, *104*, 352–4. Wax, M. J.; Stryker, J. M.; Buchanan, J. M.; Kovac, C. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 1121–2.

[2] Jones, W. D.; Feher, F. J. *Organometallics* **1983**, *2*, 562–3.

[3] Gault, Y.; Felkin, H.; Fillebeen-Khan, T.; Holmes-Smith, R.; Zakrzewski, J. *Tetrahedron Lett.* **1984**, *25*, 1279–82.

[4] Berry, M.; Elmitt, K.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1979**, *12*, 1950–8. Green, M. L. H. *Pure Appl. Chem.* **1984**, *56*, 47–58 and references therein.

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