Further Improvements in the Preparation of Disecondary Phosphines $PhHP(CH_2)_nPHPh$, $n = 2$, 3, and Their Tetracarbonyltungsten Complexes: Analysis of Their Multinuclear NMR Spectra

Ron S. Dickson, Patricia S. Elmes, and W. Roy Jackson*

Department of Chemistry, Monash University, Clayton, Victoria 3168, Australia

Received January 19, 1999

Summary: The disecondary phosphines $PhHP(CH_2)_nPHPh$, $n = 2, 3$, *have been prepared in high yields (80%) after short reaction times (6 h) and converted into the meso- and rac-diastereomers of* $[\{PhHP(CH_2)_nPHPh\}W(CO)_4]$, $n = 2, 3$. $^{12/13}C$ *isotope effects on* ^{31}P *shieldings and* $|^2J_{P-P}|$ *couplings have been calculated from the* ^{13}C *NMR spectra of the complexes.*

Introduction

As part of our interest in heterobimetallic catalysts, it became necessary to prepare significant amounts of the disecondary phosphines $PhHP(CH_2)_nPHPh$, $n = 2$, 3, and their tetracarbonyltungsten complexes.[1] Interest in this class of phosphines has increased in recent years in view of their use as ligands and as precursors for multidentates and macrocycles.[2]

Several alternative syntheses for disecondary phosphines are known.[3] Recent research on the method of lithium cleavage of ditertiary phosphines indicates that improved yields of disecondary phosphines $PhHP(CH_2)_nPHPh$ (**1**; $n = 2-4$, 6) are obtained when the reaction temperature is lowered to 0 °C.[4] Unfortunately, reducing the reaction temperature to minimize $P-CH_2$ bond cleavage and subsequent formation of Ph_2PH increases reaction times significantly (200 h for $n = 2$). Ultrasonic irradiation of diphosphines with lithium at 0 °C has been reported to accelerate the reductive cleavage without any contamination from side reactions and has been used for small-scale (300 mg) preparations of bis(alkylphenylphosphino)alkanes.[5]

We have prepared the disecondary phosphines $PhHP(CH_2)_nPHPh$ (**1**; $n = 2$, 3) in high yields (80%), faster and more conveniently than previously reported.[4] In addition, our reactions of these phosphines with tungsten hexacarbonyl have produced colorless, purer complexes than previously isolated[4] and allowed the separation and identification of all *meso* and *racemic* diastereomers on a multigram scale. Multinuclear NMR spectra are reported for all diastereomers and $|^2J_{P-P}|$ couplings obtained by computer analysis of $^{13}C\{^1H\}$ NMR spectra. $^{12/13}C$ isotope effects on $\delta(^{31}P)$ are observed in the ^{13}C NMR spectra of the tungsten complexes and measured for α-CH_2 and equatorial carbonyl carbon atoms.

Results and Discussion

Disecondary Diphosphines. The disecondary phosphines 1,2-bis(phenylphosphino)ethane and 1,3-bis(phenylphosphino)propane were prepared by a double cleavage of P−Ph bonds of the appropriate bis(diphenylphosphino)alkane with lithium under ultrasonic irradiation, followed by aqueous hydrolysis of the bis(lithium phenylphosphide) and purification by distillation. We have found a combination of ultrasonic irradiation, low reaction temperature (10 °C), and an excess of lithium very effective for the synthesis of disecondary phosphines on a multigram scale in high yields (>80%) after short reaction times (<6 h). (See Scheme 1.) $^{31}P\{^1H\}$ NMR spectroscopy showed both reaction products to be an equimolar mixture of *racemic* (RR,SS) and *meso* (RS) diastereomers. Each pair of diastereomers has been separated by *cis* coordination to tungsten carbonyl.

Diphosphine Tungsten Tetracarbonyl Complexes. The reaction of tungsten hexacarbonyl with 1,2-bis(phenylphosphino)ethane (**1**; $n = 2$) in toluene at 160 °C resulted in a clear yellow solution showing only two components, in equal amounts, by ^{31}P NMR at δ 4.9 and δ 2.5. Both *meso* and *racemic* forms of $[\{PhHP(CH_2)_2PHPh\}W(CO)_4]$ crystallized from toluene as analytically pure, colorless crystals with different morphologies. By contrast, $[\{PhHP(CH_2)_2PHPh\}W(CO)_4]$ diastereomers isolated from the same reactants heated under reflux in diglyme were reported as impure brown crystals with lower melting points.[4] The *racemic* (RR/SS) diastereomer (**3**; $n = 2$) crystallized first and was identified by the presence of two ^{13}CO resonances in the $^{13}C\{^1H\}$ NMR spectrum, whereas the *meso* (RS) diastereomer (**2**; $n = 2$) displayed three ^{13}CO resonances.

^{31}P NMR of an aliquot from the reaction of 1,3-bis(phenylphosphino)propane (**1**; $n = 3$) with tungsten hexacarbonyl in toluene at 160 °C indicated the presence of four products. Single phosphorus resonances at δ −34.1 and δ −30.4 from the expected diastereomers were obtained in a 1.3:1 ratio as 54% of the total P, as well as two multiplets attributed to polymeric products at δ −24.5 and δ −15.5 in a 1:2.9 ratio and 46% of the total P. Repetition of this reaction afforded the same products in different ratios. The solution deposited

---

[1] Dickson, R.S.; Elmes, P. S.; Fallon, G. D.; Jackson, W. R. *Organometallics*, submitted for publication.

[2] Steltzer, O.; Langhans, K. P. In *The Chemistry of Organophosphorus Compounds;* Hartley, F. R., Ed.; Wiley: New York, 1990; Vol. 1, Chapter 8.

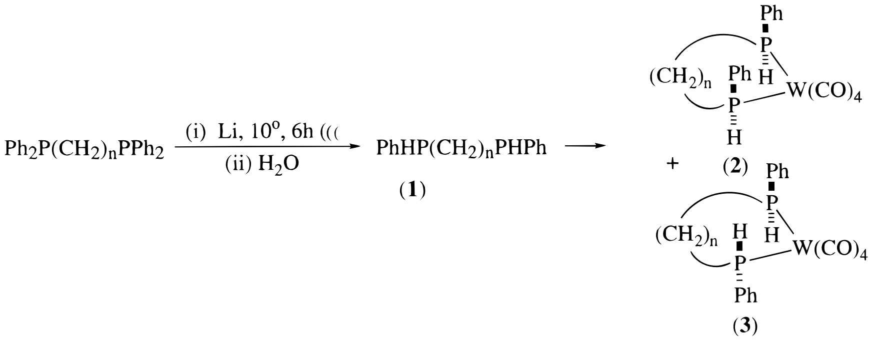
[3] Kosolapoff, G. M.; Maier, L. *Organic Phosphorus Compounds;* Wiley-Interscience: New York, 1972; Vol. 1, p 17.

[4] Kimpton, B. R.; McFarlane, W.; Muir, A. S.; Patel, P. G.; Bookham, J. L. *Polyhedron* **1993**, *12*, 2525.

[5] Chou, T.; Tsao, C.; Hung, S. C. *J. Org. Chem.* **1985**, *50*, 4329.

10.1021/om990027v CCC: $18.00

Scheme 1



hexagonal crystals of analytically pure *meso*-[{(*RS*)-$PhHP(CH_2)_3PHPh$}$W(CO)_4$] (**2**; *n* = 3) (98% isomeric purity) again identified by three resonances in the ^{13}C NMR spectrum. Isomeric purity was increased to 99.5% (^{31}P NMR analysis) by flash chromatography. The *rac*-[{(*RR*/*SS*)$PhHP(CH_2)_3PHPh$}$W(CO)_4$] complex (**3**; *n* = 3), which was less readily isolated, was obtained as a white solid in 85% isomeric purity and identified by the presence of two ^{13}CO resonances.

NMR Analysis. The $^{31}P\{^1H\}$ NMR spectrum for each of the diastereomeric tungsten carbonyl complexes consists of a single resonance flanked by ^{183}W satellites. A downfield shift of the ligand P resonances of ca. 50 ppm for the five-membered chelate rings (^{31}P NMR: δ 2.5 (*meso*), 4.9 (*racemic*)) and of ca. 20 ppm for the six-membered rings (^{31}P NMR: δ −30.4 (*meso*), −33.9 (*racemic*)) was observed on chelation (^{31}P NMR: ca. δ −46 for 1,2-diphosphine, ca. δ −53 for 1,3-diphosphine). Similar large downfield shifts have been observed previously on forming five-membered chelates.[6]

The $^{13}C\{^1H\}$ NMR spectra of the complexes display symmetrical six-line multiplets for the α-CH_2 groups and equatorial carbonyls (**2** and **3**; *n* = 2) and symmetrical five-line multiplets with unresolved central lines for the equatorial carbonyls (**2** and **3**; *n* = 3) and *ipso*, *ortho*, and *meta* phenyl-ring carbons. Computer simulation of the spectra as the X spectra of an ABX spin system[7] (A, B = ^{31}P, X = ^{13}C) yielded $|J_{P-P}|$ and $|J_{P-C}|$ coupling constants as well as the chemical shift differences $\nu_o\delta_{AB}$ arising from the $^{12/13}C$ isotopic substitution, viz., $^{12}C-P_A-W-P_B-^{13}C$. The results have been submitted as Supporting Information.

The $^2J_{P-P}$ coupling of 6.4 Hz calculated for each of the *meso*- and *rac*-[{$PhHP(CH_2)_2PHPh$}$W(CO)_4$] (**2** and **3**; *n* = 2) diastereomers is considerably less than the couplings of 20.5 and 26.5 Hz computed for *meso*- and *rac*-[{$PhHP(CH_2)_3PHPh$}$W(CO)_4$] (**2** and **3**; *n* = 3) and differ from the literature values of 12.6, 14.9, and 14.5 for *meso*- and *rac*-[{$PhHP(CH_2)_2PHPh$}$W(CO)_4$] and *meso*-[{$PhHP(CH_2)_3PHPh$}$W(CO)_4$], respectively.[4] They are instead very similar in magnitude to the $^2J_{P-P}$ couplings of +5.5 and −21.5 reported for the analogous tertiary phosphine chelates [{$Ph_2P(CH_2)_2PPh_2$}$W(CO)_4$] and [{$Ph_2P(CH_2)_3PPh_2$}$W(CO)_4$], respectively.[8] The sensitivity of these P−P couplings to ring size suggests a significant C backbone contribution. $^1J_{W-P}$ couplings of 223 and 213 for the disecondary phosphine five- and six-membered chelate rings also parallel trends found for the analogous ditertiary phosphine chelates, where $^1J_{W-P}$ decreases from 229 to 222 as chelate ring size increases from 5 to 6.

The magnitude of the chemical shift difference at P ($\nu_o\delta$) due to $^{12}C-P_A-W-P_B-^{13}C$ isotopic substitution was estimated for the ligand (**1**; *n* = 2) and for the complexes (**2** and **3**, *n* = 2 and 3). The values for the ligand were 3.5 Hz at CH_2 and 2.4 Hz at the *ipso*-phenyl C for spectra recorded at 100.6 MHz and are comparable to the values of 4.5 and 4.2 Hz recorded previously at 125.8 MHz.[4] All of the complexes gave smaller values of $\nu_o\delta$, viz., 1.15−1.3 Hz at the α-CH_2 (**2** and **3**; *n* = 2, 3), and 0.9 Hz at the equatorial CO carbons (**2** and **3**; *n* = 2). These represent $^{12/13}C$ isotope effects upon $\delta(^{31}P)$ of 0.007−0.008 ppm for the directly bonded CH_2 groups and of 0.004 ppm for the equatorial carbonyl carbons in the complexes.

Experimental Section

General Procedures. All operations involving secondary phosphine ligands and solutions of their tungsten complexes were carried out under an atmosphere of dry, oxygen-free argon or nitrogen using dry, deoxygenated solvents. Ditertiary phosphines and lithium wire (99.9%) were purchased from Aldrich. Tetrahydrofuran (THF) was distilled from Na/benzophenone prior to use. Ultrasonic reactions were performed using a conventional cleaning bath (Branson B2200 E2, output 60 W).

NMR spectra were measured at field strengths of 4.7 and 9.4 T on Bruker AC200 or DRX400 spectrometers, respectively. The ^1H NMR spectra were measured at 200 or 400 MHz, ^{13}C at 100.6 MHz, and ^{31}P at 162 MHz. Chemical shifts are referenced from Me_4Si for ^1H and ^{13}C and from 85% H_3PO_4 for ^{31}P; in all cases, a positive chemical shift denotes a shift to higher frequency. N is the splitting of the principal doublet of the signals in the $^{13}C\{^1H\}$ NMR. Iterative calculations and simulated NMR spectra were performed on an Aspect 3000 computer using the PANIC program from Bruker. PANIC is a minicomputer version of the LAOCOON[9] type programs.

Synthesis of 1,2-Bis(phenylphosphino)ethane (1; *n* = 2). In a typical procedure, a mixture of 1,2-bis(diphenylphosphino)ethane (7.90 g, 19.8 mmol) and freshly cut Li wire (1.40 g, 200 mmol) in THF (250 mL) contained in a double-walled flask with the outer jacket containing ethylene glycol was irradiated in an ultrasonic bath maintained at 10 °C by addition of crushed ice.[10] The reaction was monitored by TLC (alumina, hexane/ethyl acetate, 9:1) and was complete in 5 h.

---

(6) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

(7) Emsley, J. W.; Feeney, J.; Sutcliffe, L. H. *High-Resolution Nuclear Magnetic Resonance Spectroscopy*; Pergamon Press: Oxford, 1965; Vol. 1, p 357.

(8) Andrews, G. T.; Colquhoun, I. J.; McFarlane, W. *Polyhedron* **1983**, *2*, 783.

(9) Castellano, S.; Bothner-By, A. R. *J. Chem. Phys.* **1962**, *36*, 1951.

The deep-red solution was cannulated from excess Li and cooled in an ice−water bath before hydrolysis with deoxygenated water (30 mL). The phosphine was extracted with diethyl ether (60 mL); the extracts were combined and washed with cold HCl (2 M, 2 × 10 mL), followed by cold water, until any acidity was completely removed. The organic layer was dried (Na_2CO_3) and filtered, and the solvent removed under reduced pressure. The residual viscous liquid was purified by Kugelrohr distillation to give the required compound as a colorless oil (3.9 g, 80%), bp (oven) 160 °C/1 mm (lit. 161 °C/0.8 mm).[11] ^{31}P{^{1}H} NMR (toluene-d_8) indicated an equimolar mixture of two diastereomers: δ −45.8, −46.4 (lit. δ −45.6, −45.9).[4] ^{1}H and ^{13}C{^{1}H} NMR data were similar to literature data.[4]

Synthesis of 1,3-Bis(phenylphosphino)propane (1; *n* = 3). In a similar manner, ultrasonic irradiation of a mixture of 1,3-bis(diphenylphosphino)propane (9.40 g, 22.8 mmol) and Li wire (1.63 g, 228 mmol) in THF (200 mL), followed by aqueous hydrolysis and Kugelrohr distillation, gave the title compound as a clear oil (5.0 g, 84%), bp (oven) 200 °C/1 mm (lit. 191−200 °C/5 mm).[12] ^{31}P{^{1}H} NMR (toluene-d_8): δ −52.8, −52.9. The two diastereomers were present in equimolar ratio, lit. δ −51.9,−52.0.[4] ^{1}H and ^{13}C{^{1}H} NMR data were similar to literature data.[4]

Synthesis of Tungsten Tetracarbonyl Complexes. These were prepared by heating tungsten hexacarbonyl with the appropriate disecondary phosphine and toluene in a sealed, evacuated, glass pressure reaction tube (100 mL) at 160 °C for 40 h. After cooling and venting, an aliquot was removed for analysis by ^{31}P NMR spectroscopy before isolation of products proceeded.

***meso/rac*-Tetracarbonyl(1,2-bisphenylphosphinoethane)tungsten (2, 3; *n* = 2).** Reaction of tungsten hexacarbonyl (2.40 g, 6.8 mmol) and 1,2-bis(phenylphosphino)ethane (1.68 g, 6.8 mmol) in toluene (5 mL) gave a clear, pale-yellow solution. The ^{31}P NMR spectrum of the crude product showed only two resonances at δ 4.9 and 2.5 of equal intensity. The solution rapidly deposited colorless platelets, which were separated, washed, dried, and identified by ^{13}C NMR as *rac*-[{(*RR*/*SS*)-PhHP(CH_2)$_2$PHPh}W(CO)$_4$] (**3**; *n* = 2). Yield: 1.24 g (34%). Mp: 176.5−178 °C. Anal. Found: C, 39.9; H, 3.0; P, 11.4. Calcd for $C_{18}H_{16}O_4P_2W$: C, 39.9; H, 3.0; P, 11.4. MS(EI): *m*/*z* 544 (^{186}W) [M$^+$]. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 4.9 (s, J_{W-P} = 222.7 Hz) and 4% *meso*-diastereomer δ 2.5. ^{1}H NMR (CDCl$_3$): δ 1.40 (m, 2H, CH$_2$), 2.87 (m, 2H, CH$_2$), 6.00 (m, 2H, J_{P-H} = 334 Hz, PH), 7.47 (m, 6H, aromatic m-H and p-H), 7.73 (m, 4H, aromatic o-H). ^{13}C{^{1}H} NMR: δ 26.7 (m, *N* = 43.0 Hz, CH$_2$), 129.1 (m, *N* = 10.3 Hz, C3, 5), 130.5 (m, *N* = 46.5 Hz, C1, *ipso*-C), 130.8 (m, *N* = 2.0 Hz, C4), 133.1 (m, *N* = 12.1 Hz, C2, 6), 200.3 (t, $^{2}J_{P-C}$ = 7.2 Hz, CO$_{ax}$), 206.6 (m, *N* = 18.3 Hz, CO$_{eq}$). IR (CH$_2$Cl$_2$) cm^{-1}: ν(CO) 2020, 1918 (sh), 1899.

A second quantity of material which crystallized from solution as opaque aggregates was filtered, washed, dried, and confirmed by ^{13}C NMR as *meso*-[{(*RS*)-PhHP(CH$_2$)$_2$PHPh}W(CO)$_4$] (**2**; *n* = 2). Yield: 0.25 g (7%). Mp: 168−9 °C. Anal. Found: C, 40.0; H, 3.0; P, 11.1. Calcd for $C_{18}H_{16}O_4P_2W$: C, 39.9; H, 3.0; P, 11.4. MS(EI): *m*/*z* 544 (^{186}W) [M$^+$]. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 2.5 (s, J_{W-P} = 222.6 Hz). ^{1}H NMR (CDCl$_3$): δ 2.04 (m, 2H, CH$_2$), 2.35 (m, 2H, CH$_2$), 6.13 (m, 2H, J_{P-H} = 337 Hz, PH), 7.46 (m, 6H, aromatic m-H and p-H), 7.69 (m, 4H, aromatic o-H). ^{13}C{^{1}H} NMR: δ 26.0 (m, *N* = 44.2 Hz, CH$_2$), 129.1 (m, *N* = 10.1 Hz, C3, 5), 130.7 (m, *N* = 2.1 Hz, C4), 130.9 (m, *N* = 43.4 Hz, C1, *ipso*-C), 132.6 (m, *N* = 11.9 Hz, C2, 6), 198.9 (t, $^{2}J_{P-C}$ = 5.7 Hz, CO$_{ax}$), 201.6 (t, $^{2}J_{P-C}$ = 8.0 Hz, CO$_{ax}$), 206.6 (m, *N* = 18.6 Hz, CO$_{eq}$). IR (CH$_2$Cl$_2$) cm^{-1}: ν(CO) 2020, 1917 (sh), 1899, 1883 (infl).

The washings and filtrate were combined and concentrated to afford further white precipitate (0.35 g, 9%). ^{31}P NMR: δ 4.9 (30.5%), δ 2.5 (69.5%). Discolored residual material containing both diastereomers in the same proportions was obtained on complete evaporation of the solvent.

***meso/rac*-Tetracarbonyl(1,3-bisphenylphosphinopropane)tungsten (2, 3; *n* = 3).** Reaction of tungsten hexacarbonyl (1.58 g, 4.5 mmol) and 1,3-bis(phenylphosphino)propane (1.16 g, 4.5 mmol) in toluene (5 mL) resulted in a clear, pale-yellow solution. ^{31}P NMR analysis of the crude product showed four phosphorus resonances at δ −34.1 (s, 30%), −30.6 (s, 24%), −24.5 (m, 12%), and −15.5 (m, 34%). Colorless hexagonal crystals which gradually deposited on cooling were separated, washed with methanol, dried under vacuum (0.01 mm), and identified by ^{13}C NMR as *meso*-[{(*RS*)-PhHP(CH$_2$)$_3$PHPh}W(CO)$_4$] (**2**; *n* = 3), mp 209.5−210 °C. Anal. Found: C, 40.95; H, 3.2; P, 10.85. Calcd for $C_{19}H_{18}O_4P_2W$: C, 41.0; H, 3.3; P, 11.1. MS(EI): *m*/*z* 558 (^{186}W) [M$^+$]. ^{31}P{^{1}H} NMR (CDCl$_3$): δ −30.4 (s, J_{W-P} = 212.1 Hz), isomeric purity 99.5%. ^{1}H NMR (CDCl$_3$): δ1.80 (m, 3H, CH$_2$), 2.46 (m, 1H, CH$_2$), 2.74 (m, 2H, CH$_2$), 5.89 (m, 2H, J_{P-H} = 328 Hz, PH), 7.44 (m, 6H, aromatic m-H and p-H), 7.64 (m, 4H, aromatic o-H). ^{13}C{^{1}H} NMR: δ 24.0 (t, $^{2}J_{P-C}$ = 1.8 Hz, β-CH$_2$), 27.4 (m, N = 27.4 Hz, α-CH$_2$), 128.9 (m, *N* = 9.8 Hz, C3,5), 130.2 (m, *N* = 1.8 Hz, C4), 132.3 (m, *N* = 11.2 Hz, C2,6), 133.4 (m, *N* = 48.3 Hz, C1, *ipso*-C), 199.3 (t, $^{2}J_{P-C}$ = 6.9 Hz, CO$_{ax}$), 203.4 (t, $^{2}J_{P-C}$ = 8.4 Hz, CO$_{ax}$), 204.8 (m, *N* = 14.1 Hz, CO$_{eq}$). IR (CH$_2$Cl$_2$) cm^{-1}: ν(CO) 2019, 1919, 1893, 1868 (sh).

Further fractional crystallization from toluene gave white precipitates which were mixtures of the *meso*/*rac*-diastereomers. ^{31}P{^{1}H} NMR: δ −30.4 (33%), δ −33.9 (67%). Removal of the toluene and addition of acetone/methanol to the residue gave an off-white precipitate of mainly *rac*-[{(RR/SS)PhHP(CH$_2$)$_3$PHC$_6$H$_5$}W(CO)$_4$]. Mp: 123−5 °C. Anal. Found: C; 40.2; H, 3.3. Calcd for $C_{19}H_{18}O_4P_2W$: C, 41.0; H, 3.3. ^{31}P{^{1}H} NMR (CDCl$_3$): δ −33.9 (s, J_{W-P} = 212.9 Hz) (88%), δ −30.4 (12%). No further purification of the *racemic* diastereomer was attempted, as the compound appeared to decompose with handling. ^{1}H NMR (CDCl$_3$): δ 2.01 (m, 2H, CH$_2$), 2.19 (m, 2H, CH$_2$), 2.38 (m, 2H, CH$_2$), 6.06 (m, 2H, J_{P-H} = 339 Hz, PH), 7.46 (m, 6H, aromatic m-H and p-H), 7.66 (m, 4H, aromatic o-H). ^{13}C{^{1}H} NMR: δ 22.0 (t, $^{2}J_{P-C}$ = 1.8 Hz, β-CH$_2$), 26.9 (m, *N* = 28.6 Hz, α-CH$_2$), 128.9 (m, *N* = 9.7 Hz, C3,5), 130.3 (m, *N* = 1.9 Hz, C4), 132.5 (m, *N* = 11.2 Hz, C2,6), 133.3 (m, *N* = 43.9 Hz, C1, *ipso*-C), 201.3 (t, $^{2}J_{P-C}$ = 7.3 Hz, CO$_{ax}$), 204.7 (m, *N* = 14.5 Hz, CO$_{eq}$).

Supporting Information Available: A table of calculated coupling constants, J_{PP} and J_{PC}, for complexes **2** and **3**, *n* = 2 and 3, as well as selected observed and simulated NMR resonances from ^{13}C{^{1}H} spectra (100.6 MHz) of [{(*RS*)-PhHP(CH$_2$)$_n$PHPh}W(CO)$_4$] diastereomers (**2**; *n* = 2, 3). This material is available free of charge via the Internet at http://pubs.acs.org.

OM990027V

---

(10) **Safety Consideration.** Reactions involving lithium metal and immersion in an ultrasonic bath containing water should not be carried out using single-walled flasks for fear of breakage.

(11) Issleib, K.; Weidmann, H. *Chem. Ber.* **1968**, *101*, 2197.

(12) Issleib, K.; Jacob, D. *Chem. Ber.* **1961**, *94*, 107.