3 was also a product of the pyrolysis of 7, but in that case 2 and 5 were more prominent products. In the pyrolysis of 1, trapping of $Me_2Si{=}SiMe_2$ by butadiene provides evidence for reaction 20 and, hence, for reaction 19 in Scheme III, but reaction 25 is clearly minor compared to reaction 18. A possible explanation of the difference is that elimination of Me_3SiH from 6 occurs entirely at silicon centers, as in reaction 8, whereas with 7 a carbon center is involved. Butadiene trapping also gave evidence for Me_2Si:, probably formed in reactions 26 and 27 as well as

$$Me_3SiSiMe_2^{\bullet} + RH \rightarrow Me_3SiSiMe_2H \rightarrow Me_2Si\colon + Me_3SiH \quad (26)$$

$$Me_3SiSi(Me_2)SiMe_3 \rightarrow Me_2Si\colon + Me_3SiSiMe_3 \quad (27)$$

reaction 22. Reaction 27 might also be a source of the product 4, but the main route to 4 is likely to be self-combination of $Me_3Si^{\bullet}$ radicals. We failed to trap $Me_2Si{=}CH_2$ with butadiene because reactions 16 and 23 are fast, whereas the rate constant for the reaction of $Me_2Si{=}CH_2$ with butadiene is relatively low.[5]

Our evidence in support of Scheme II prompted us to speculate that the similar reaction sequence shown in Scheme IV might be important in the pyrolysis of 4 as a route to the disilacyclobutane 5, which is a major product at low pressure.[4] However, on testing these ideas by synthesizing and pyrolyzing compound 8, we found that it was more stable thermally than compound 4 and gave little 5 when pyrolyzed under the conditions used for 4. Structurally, 8 resembles 7 rather than 6, with the additional drawback that a higher ring strain would have to be overcome in reaction 36 than in reaction 25 or 18. We conclude that elimination of Me_3SiH to form a stable cyclic product is a feasible and potentially important reaction in those polycarbosilanes that have the appropriate silicon–carbon skeleton, i.e. where the components of Me_3SiH are attached exclusively to silicon.

In the pyrolysis of 1, the pronounced pressure dependence of product composition revealed by comparison of this work with that of Barton[3] has close parallels in similar organosilicon pyrolyses. In the pyrolysis of 4, product 5 was more important than product 9 (see Scheme IV) at low pressure,[4] but the position is totally reversed at high pressure,[10] because at low pressure the unimolecular radical dissociation reactions (29) and (31) are favored over the bimolecular reaction (33); increasing the pressure increases the relative importance of reaction 33. A similar situation arises in the pyrolysis of 3, where the main product at low pressure is 5,[11] while at high pressure it is 1,1,3,3,5-pentamethyl-1,3,5-trisilacyclohexane,[12] a product that bears the same relationship to 3 as 9 bears to 4. An explanation along similar lines, involving the balance between unimolecular reactions 4 and 5 on the one hand and bimolecular reactions 16 and 17 on the other, accounts for the different results observed by Barton[3] and by us.

Acknowledgment. We are most grateful to Dr. Peter Lo of Dow Corning Sussex Research for his generous help and encouragement. We thank Geraint H. Morgan for help with the pyrolysis experiments and the SERC for support.

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Regiospecific Nickel Cyanide and Phase Transfer Catalyzed Synthesis of β,γ-Unsaturated Acids from Allenes

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Summary: Allenes react with carbon monoxide in an aqueous base–toluene two-phase system, with cetyltrimethylammonium bromide as the phase-transfer agent and nickel cyanide as the metal catalyst, to give β,γ-unsaturated acids in 48–66% yields. This reaction proceeds under exceptionally mild conditions (90 °C, 1 atm), with the regiochemistry being opposite to that previously observed in hydrocarboxylation reactions.

A variety of metal-complex-catalyzed reduction, oxidation, and carbonylation reactions occur under remarkably mild conditions with use of phase-transfer catalysis.[1,2] Research in carbon monoxide phase-transfer processes has focused on the use of palladium, cobalt, and, to a lesser extent, iron complexes as catalysts for the conversion of halides to acids. More economical than any of these transition-metal complexes is the use of nickel compounds as catalysts. The cyanotricarbonylnickelate anion, generated by the phase-transfer-catalyzed reaction of nickel cyanide, carbon monoxide, and base, is an effective catalyst for the production of acids (eq 1) from allyl halides,[3] iodoarenes,[4] and benzyl chlorides (lanthanide salts promote this reaction).[5]

$$RX + CO \xrightarrow[C_6H_6,\ NaOH,\ 60\text{–}90\ ^\circ C,\ 1\ atm]{R_4N^+X^-,\ Ni(CN)_2{\cdot}4H_2O} RCOOH \quad (1)$$

A conceptually different type of carbonylation reaction is that which involves the addition of carbon monoxide and water (i.e., hydrocarboxylation) or alcohol (i.e. hydroesterification) to an unsaturated substrate. The homogeneous hydrocarboxylation and hydroesterification of allenes, catalyzed by a variety of metal complexes under stringent conditions, results in the formation of α,β-unsaturated acids or esters in low to moderate yields.[6,7] These reactions are believed to proceed via vinylmetallic complexes. Alkoxycarbonylation of allenes, which occurs under mild conditions with use of palladium chloride as the catalyst in alcohol solution, also affords the α,β-unsaturated carbonyl product.[8,9] To our knowledge there

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[5] Amer, I.; Alper, H. *J. Am. Chem. Soc.* **1989**, *111*, 927.

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[9] For an intramolecular version, see footnote 4 of: Lathbury, D.; Vernon, P.; Gallagher, T. *Tetrahedron Lett.* **1986**, *27*, 6009.

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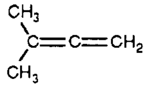
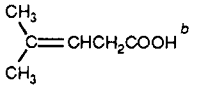
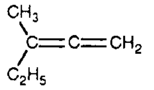
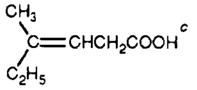
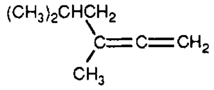
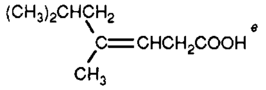
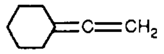
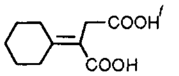
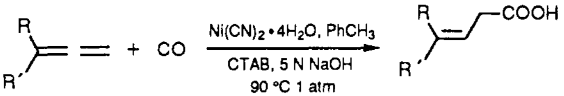
Table I. Nickel and Phase Transfer Catalyzed Carbonylation of Allenes

allene	reactn time, h	product[a]	yield, % GC	yield, % isolated
 $(CH_3)_2C{=}C{=}CH_2$	6	 $(CH_3)_2C{=}CHCH_2COOH$[b]	65	52
 $(CH_3)(C_2H_5)C{=}C{=}CH_2$	10	 $(CH_3)(C_2H_5)C{=}CHCH_2COOH$[c]	80	58
$CH_3CH_2CH{=}C{=}CH_2$	10	$C_2H_5CH{=}CHCH_2COOH$[d]	60	48
 $((CH_3)_2CHCH_2)(CH_3)C{=}C{=}CH_2$	10	 $((CH_3)_2CHCH_2)(CH_3)C{=}CHCH_2COOH$[e]	80	66
	10	 [f]	95	72

[a] The structures of the products were determined by comparison of physical and spectral data with those for authentic samples. [b] Reference 10. [c] Reinheckel, H.; Sonnek, G.; Gensike, R. *J. Prakt. Chem.* **1975**, *317*, 273. [d] Birch, A. J.; Slobbe, J. *Aust. J. Chem.* **1976**, *29*, 2737. [e] ^1H NMR ($CDCl_3$): δ 0.81 (d, ($CH_3)_2$CH), 1.58 (s, CH_3), 1.75 (d, CH_2CH), 1.90 (m, CH($CH_3)_2$), 3.02 (d, CH_2CH=), 5.32 (m, CH=), 10.56 (s (br), COOH). ^{13}C NMR ($CDCl_3$): δ 17.5, 22.1 (CH_3), 25.8 (CH($CH_3)_2$), 26.0 (CH_2CH), 33.4 (CH_2COOH), 116.2 (CH=), 138.9 (>C=), 179.0 (COOH). MS: *m/e* 156 [M]$^+$. [f] ^1H NMR ($CDCl_3$): δ 1.50, 2.18, 2.58, 3.16 (m each, methylene protons). ^{13}C NMR ($CDCl_3$): δ 25.9, 27.7, 28.0, 31.7, 31.9 (ring methylene carbons), 34.8 (CH_2COOH), 118.8, 152.2 (olefinic carbons), 169.3, 172.2 (carbonyl carbons). MS: *m/e* 180 [M − H_2O]$^+$. Mp 175.3–176.6 °C (lit. mp 177–179 °C): Noji, T.; Tsuji, J. *Tetrahedron* **1969**, *25*, 4099.

are no examples of the regioselective hydrocarboxylation of allenes to β,γ-unsaturated carbonyl compounds. We now wish to report that the nickel cyanide phase-transfer system is of genuine utility for the regiospecific net hydrocarboxylation of allenes to β,γ-unsaturated acids under exceptionally mild conditions.

Treatment of a toluene solution of 3-methyl-1,2-butadiene (**1**; R = R′ = CH_3) with carbon monoxide, 5 N sodium hydroxide, cetyltrimethylammonium bromide (CTAB) as the phase-transfer agent, and hydrated nickel cyanide as the metal catalyst, for 6 h at 90 °C and 1 atm, afforded 4-methyl-3-pentenoic acid (**2**, R = R′ = CH_3)[10] in a 52% yield of analytically pure material (crude yield was 65%). The ratio of substrate to nickel catalyst used was 10:1, while the optimum proportion of nickel cyanide to CTAB was 5:1. No other products were formed in this reaction. Also, only 6% of **2** (R = R′ = CH_3) is formed when the reaction is effected in the absence of the quaternary ammonium salt. Therefore, the reaction is a genuine phase-transfer process.

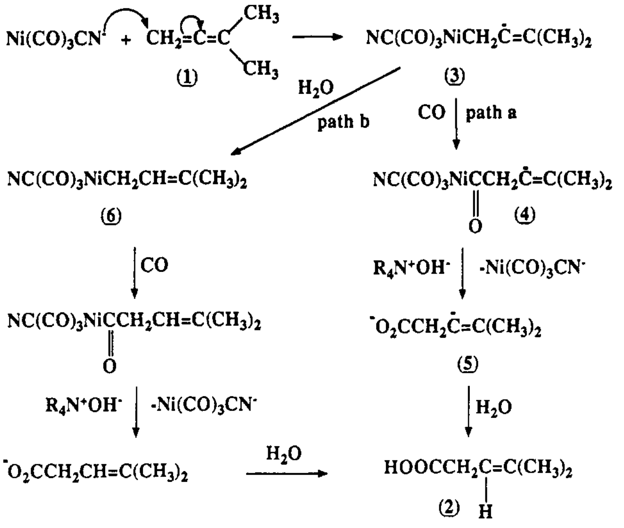


1 2

This simple hydrocarboxylation reaction is applicable to other disubstituted and monosubstituted allenes, giving β,γ-unsaturated acids in reasonable yields (see Table I for results). In the case of pentamethyleneallene, an unsaturated acid is formed.

Possible pathways for the reaction are outlined in Scheme I (illustrated for **1**, R = R′ = CH_3). Attack of the in situ generated cyanotricarbonylnickelate anion at the least substituted terminal carbon of the allene would give the vinyl carbanion **3**.[11] Carbon monoxide insertion (path a) would afford the acylnickel complex **4**, which on hydroxide ion cleavage of the carbon–nickel bond would generate the dianion **5**. The β,γ-unsaturated acid **2** would then arise by protonation of **5**. It is, of course, also possible that protonation of **3** to **6** can occur prior to carbon monoxide insertion (path b).

Scheme I



The following general procedure was used: to degassed toluene (20 mL) and 5 N NaOH (20 mL) was added, under a carbon monoxide atmosphere, 0.182 g (1.0 mmol) of $Ni(CN)_2 \cdot 4H_2O$ and 0.07 g (0.20 mmol) of CTAB. The reaction mixture was stirred at 90 °C for 1 h, a toluene (10 mL) solution of the allene (10 mmol) was added in small portions (over a 1-h period), and stirring was then continued at 90 °C for the time indicated in Table I (the reaction was followed by gas chromatography). The mixture was cooled to room temperature, the phases were separated, and the aqueous phase was neutralized with 10% HCl and then extracted with ether. The ether extract was dried (Na_2SO_4) and concentrated, affording **2**. Pure acid was isolated by silica gel column chromatography with hexane/ethyl acetate as the eluant.

In conclusion, nickel cyanide is an active catalyst for the regiospecific conversion of allenes to β,γ-unsaturated acids under phase-transfer conditions. β,γ-Unsaturated acids

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(11) Attack at the same carbon atom of the allene occurs on reaction with Grignard reagents in the presence of copper(I) salts: Gelin, R.; Albraud, M. *C. R. Seances Acad. Sci.* **1976**, *283C*, 755.

286 *Organometallics* **1990**, *9*, 286–288

are valuable precursors to a variety of cyclic compounds, including iodolactones[10] and α,β-unsaturated γ-lactones.[12]

Acknowledgment. We are grateful to British Petroleum and to the Natural Sciences and Engineering Research Council of Canada for support of this research.

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Organotransition-Metal Complexes of Multidentate Ligands. 11. Synthesis, Structure, and Reactivity of the First Intramolecular Coordination Compound with a Weakly Bound η^2-Arene[1]

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Summary: Thermolysis of (PhHCPz'$_2$)Mo(CO)$_4$ (**1**) in DME gives (PhHCPz'$_2$)Mo(CO)$_3$ (**2**) (Pz' = 3,5-dimethylpyrazol-1-yl); comparison of the structural details of the two compounds and the reactivity of **2** show that this compound is the first example containing an intramolecularly coordinated η^2-arene ligand.

Though the intramolecular η^2-bound arenes of transition metals were proposed 19 years ago as plausible intermediates prior to the activation of the aromatic carbon–hydrogen bonds, which is often referred to as "ortho metalation",[2] all the reports concerning the activation available today center on the intermolecular η^2-bound ligands.[3] If difficulty in isolating the intermediates can be attributed to the facile formation of a nearly unstrained four- or five-membered ring through the proximity effect,[4] suitable adjustments may bring an electrophilic center close sterically to one π-bond of a more distant phenyl fragment so that the internal η^2-arene intermediates can be isolated by virtue of the high kinetic or thermodynamic energy barrier which may be required for converting the intermediates into the unfavorable six-or-more-membered ortho metalated complexes (Scheme I). Since the electron-deficient compound (H$_2$CPz'$_2$)Mo(CO)$_3$ (Pz' = 3,5-dimethylpyrazol-1-yl) is apparently involved as an intermediate in the formation of the product compound [(H$_2$CPz'$_2$)Mo(CO)$_3$]$_2$, obtained from thermolysis of (H$_2$CPz'$_2$)Mo(CO)$_4$,[1c] this recognition has prompted us to attempt to isolate the intermediates using the bulkier bidentate ligands RR'CPz'$_2$ with R = R' = arene. We hope that the larger ligand would impede dimerization of the intermediates and increase the probability of a bonding interaction between one π-bond of an arene in RR'CPz'$_2$ and the electron-deficient metal center. Here we wish to report our preliminary results showing that the first intramolecular coordination compound with a weakly bound η^2-arene is indeed isolable by application of the strategy. We believe that it may have general applicability in the preparation of the intramolecular η^2-arene compounds, the probable precursors leading to the ortho metalated complexes. Furthermore, our results also imply that the intramolecular attachment of an η^2-arene can prevent the reported replacement of the binding arene by stronger nucleophiles in the [Os(NH$_3$)$_5$(η^2-arene)]$^{2+}$ complexes.[3b]

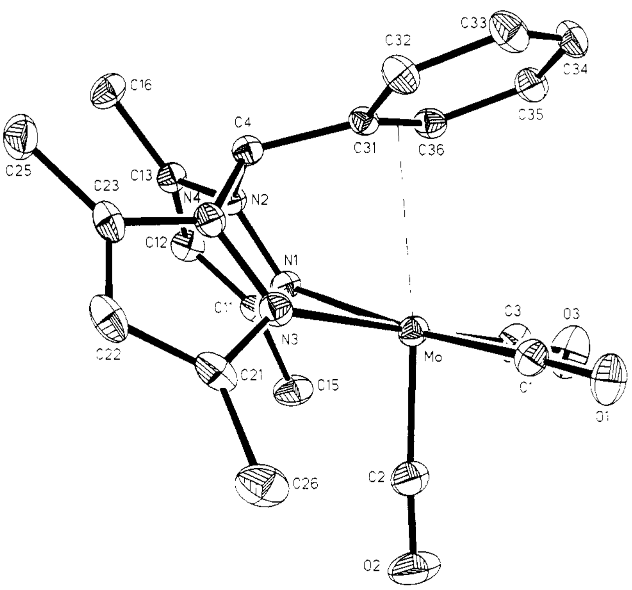

Figure 1. Structure of (PhHCPz'$_2$)Mo(CO)$_3$ (**2**) illustrating the atomic numbering scheme. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and bond angles (deg) are as follows: Mo–C(1), 1.941 (4); Mo–C(2), 1.897 (5); Mo–C(3), 1.928 (5); Mo–N(1), 2.292 (3); Mo–N(3), 2.265 (3); C(31)–C(32), 1.394 (6); C(32)–C(33), 1.377 (6); C(33)–C(34), 1.378 (7); C(34)–C(35), 1.360 (6); C(35)–C(36), 1.395 (6); C(36)–C(31), 1.402 (6); Mo···C(31), 2.766 (4); Mo···C(36), 2.840 (4); ∠C(1)–Mo–C(3), 86.8 (2); ∠N(1)–Mo–N(3), 79.5 (1); ∠Mo–N(1)–N(2), 115.6 (2); ∠Mo–N(3)–N(4), 116.4 (2); ∠N(1)–N(2)–C(4), 117.0 (3); ∠N(3)–N(4)–C(4), 116.7 (3).

Thermolysis of (PhHCPz'$_2$)Mo(CO)$_4$ (**1**) in DME induced decarbonylation, giving (PhHCPz'$_2$)Mo(CO)$_3$ (**2**),[5]

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(1) (a) Part 1: Shiu, K.-B.; Vong, W.-J. *J. Chin. Chem. Soc. (Taipei)* **1987**, *34*, 195. (b) Part 2: Shiu, K.-B.; Chang, C.-J. *Ibid.* **1987**, *34*, 297. (c) Part 3: Shiu, K.-B.; Liou, K.-S. *Ibid.* **1988**, *35*, 187. (d) Part 4: Shiu, K.-B.; Lee, L.-Y. *J. Organomet. Chem.* **1988**, *348*, 357. (e) Part 5: Shiu, K.-B.; Chang, C.-J.; Wang, Y.; Cheng, M.-J. *J. Chin. Chem. Soc. (Taipei)* **1989**, *36*, 25. (f) Part 6: Shiu, K.-B.; Lee, L.-Y. *Ibid.* **1989**, *36*, 31. (g) Part 7: Shiu, K.-B.; Liou, K.-S.; Cheng, C. P.; Fang, B.-R.; Wang, Y.; Lee, G.-H.; Vong, W.-J. *Organometallics* **1989**, *8*, 1219. (h) Part 8: Shiu, K.-B.; Liou, K.-S.; Wang, S.-L.; Cheng, C. P.; Wu. F.-J. *J. Organomet. Chem.* **1989**, *359*, C1. (i) Part 9: Shiu, K.-B.; Shen, F.-M.; Wang, S.-L.; Wei, S.-C. *Ibid.* **1989**, *372*, 251. (j) Part 10: Shiu, K.-B.; Liou, K.-S.; Wang, S.-L.; Wei, S.-C. *Organometallics*, in press.

(2) Parshall, G. W. *Acc. Chem. Res.* **1970**, *3*, 139.

(3) (a) Harman, W. D.; Sekine, M.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 5725 and references cited therein. (b) Harman, W. D.; Taube, H. *Ibid.* **1988**, *110*, 7555.

(4) (a) Parshall, G. W. *Catalysis (London)* **1977**, *1*, 335. (b) Bruce, M. I. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 73. (c) Newkome, G. R.; Puckett, W. E.; Gupta, V. K.; Kiefer, G. E. *Chem. Rev.* **1986**, *86*, 451. (d) Omae, I. *J. Organomet. Chem. Libr.* **1986**, *18*, 1; *Coord. Chem. Rev.* **1988**, *83*, 137.

(5) (a) Preparation of **1**: A solution containing PhHCPz'$_2$ (1.27 g, 4.55 mmol) and Mo(CO)$_6$ (1.18 g, 4.47 mmol) in DME (30 mL) was refluxed for 1.5 h. The solvent was then removed under vacuum. Recrystallization of the solid residue from CH$_2$Cl$_2$/hexane produced yellow-green blocks of **1** in typical yields of 85%. Anal. Calcd for C$_{21}$H$_{20}$MoN$_4$O$_4$: C, 51.64; H, 4.14; N, 11.47. Found: C, 51.66; H, 4.13; N, 11.52. ^{1}H NMR (23 °C, acetone-d_6, 100 MHz): δ 7.77 (s, 1 H), 7.35 (m, 3 H), 6.39 (m, 2 H), 6.32 (s, 2 H), 2.63 (s, 6 H), 2.54 (s, 6 H), ppm. IR (CH$_2$Cl$_2$): ν_{CO} 2016 (m), 1898 (s), 1868 (s), 1820 (s) cm^{-1}. IR (KBr): ν_{CO} 2016 (m), 1882 (s), 1860 (s), 1816 (s) cm^{-1}. (b) Preparation of **2**: A solution of **1** (3.0 mmol) in DME (50 mL) was refluxed for 70 h, giving an orange-yellow suspension. The suspension was cooled and filtered and the residue washed with 5 mL of CH$_2$Cl$_2$ and dried, yielding 1.22 g (88%). Anal. Calcd for C$_{20}$H$_{20}$MoN$_4$O$_3$: C, 52.18; H, 4.38; N, 12.17. Found: C, 51.85; H, 4.43; N, 12.12. ^{1}H NMR (23 °C, CD$_2$Cl$_2$, 100 MHz): δ 7.53 (m, 3 H), 7.07 (s, 1 H), 6.56 (m, 2 H), 6.05 (s, 2 H), 2.45 (s, 12 H) ppm. IR (CH$_2$Cl$_2$): ν_{CO} 1918 (s), 1798 (vs) cm^{-1}. IR (KBr): ν_{CO} 1914 (s), 1802 (s), 1770 (s) cm^{-1}.

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