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# Conformational preferences in transition-metal carbenes

M. M. Francl, W. J. Pietro, R. F. Hout Jr., and W. J. Hehre

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counting statistics and included a term $(0.025)^2$, where $S$ is the scan count. Non-hydrogen atoms were refined anisotropically; hydrogen atoms were located in difference maps and included as fixed contributions with isotropic $B = 6.0$ Å$^2$.

Both enantiomorphs were refined independently, and the correct choice is unambiguous. The refinement of the $S,S$ isomer yielded $R = 0.061$, $R_w = 0.075$, and GOF = 2.267 and had 33 reflections for which $\Delta F > 5\sigma(F_o)$. The $R,R$ isomer yielded $R = 0.039$, $R_w = 0.044$, and GOF = 1.334 and had only one such reflection. The improvement in $R_w$ is approximately seven times that necessary to distinguish the correct enantiomer with 99.5% probability of the Hamilton $R$ factor ratio test,[22] and thus the $R,R$ absolute configuration is shown to be correct. The maximum residual in a final difference map was 0.56 e Å$^{-3}$, associated with the Br position.

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**Registry No.** (*S*)-Si(*R*)-1, 85067-20-5; (*R*)-Si(*S*)-1, 85067-21-6; **1a**, 85082-06-0; **1b**, 85067-10-3; (*R*)-Si(*R*)-(−)-**2**, 85067-12-5; (*R*)-Si(*S*)-**2**, 85067-11-4; (*R*)-(+)-**3**, 1025-08-7; (*S*)-(+)-**4**, 22368-85-0; (*S*)-(+)-**5**, 85067-13-6; (*S*)-(+)-**6**, 85067-14-7; **7**, 16116-99-7; (*S*)-**8**, 32147-43-6; (*S*)-(−)-**9**, 960-82-7; (*R*)-Si(*R*)-**10**, 85067-15-8; (*R*)-Si-(*S*)-**10**, 85067-18-1; (*R*)-Si(*R*)-**11**, 85067-16-9; (*R*)-Si(*S*)-**11**, 85067-19-2; (*R*)-(−)-**12**, 85114-69-8; (*R*)-(−)-**13**, 85067-17-0; $Cl_3CCO_2Na$, 650-51-1; bromochloromethane, 74-97-5; dibromomethane, 74-95-3.

**Supplementary Material Available:** Complete listings of atomic coordinates and anisotropic thermal parameters, hydrogen atom coordinates, and observed and calculated structure factors (13 pages). Order information is given on any current masthead page.

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(21) Frenz, B. A.; Okaya, Y. Enraf-Nonius Structure Determination Package, Enraf Nonius, Delft, Holland 1980.

(22) Hamilton, W. C. *Acta Crystallogr.* **1965**, *18*, 502.

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# Conformational Preferences in Transition-Metal Carbenes

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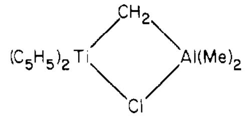
*Received November 2, 1982*

The equilibrium structures and conformational preferences of titanium and zirconium methylidene complexes have been examined by using ab initio molecular orbital theory. All systems considered prefer planar arrangements. For highly electron-deficient methylidenes, perpendicular forms are 10–20 kcal mol$^{-1}$ higher in energy; this difference increases with increasing saturation of the metal center. While these barriers to rotation in main-group olefin analogues (which are generally much larger) may be related to $\pi$-bond strengths, it is shown that such a relationship is not appropriate for bonds involving transition metals.

## Introduction

Transition-metal carbene complexes are known to participate in, or have been implicated in, numerous organometallic reactions.[2] Tantalum, chromium, molybdenum, and tungsten carbenes have been extensively characterized, as have compounds incorporating double bonds between carbon and many of the later transition metals.[3] Transition metal to carbon triple bonds have also been observed.[4] This situation is in direct contrast to that for compounds incorporating multiple bonds to heavy main-group elements, few of which are stable. In addition to their potential utility as catalytic agents then, these species are of interest in understanding the chemistry of their main-group analogues.

At present, there is no example of an isolable metal carbene involving a group 4 metal (titanium, zirconium, or hafnium). Adducts with Lewis acids are known., e.g., the Tebbe reagent[5]



These exhibit behavior consistent with that expected for free carbenes, for example, catalysis of olefin metathesis and methylenation. Little is known about the structures and stabilities of the free species.[6]

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(1) (a) Chevron Fellow. (b) National Science Foundation Predoctoral Fellow.

(2) For a discussion see: J. P. Collman and L. S. Hegedus, "*Principles and Applications of Organotransition Metal Chemistry*", University Science Books, Mill Valley, CA, 1980.

(3) For reviews, see: (a) F. J. Brown, *Prog. Inorg. Chem.*, **27**, 1 (1980), and references therein; (b) R. R. Schrock, *Acc. Chem. Res.*, **12**, 98 (1979).

(4) (a) E. O. Fischer, G. Kreis, C. G. Kreiter, J. Müller, G. Huttner, and H. Lorenz, *Angew. Chem., Int. Ed. Engl.*, **12**, 564 (1973); (b) G. Huttner, H. Lorenz, and W. Gartzke, *ibid.*, **13**, 609 (1974); (c) L. J. Guggenberger and R. R. Schrock, *J. Am. Chem. Soc.*, **97**, 2935 (1975); (d) S. J. McLain, C. D. Wood, L. W. Messerle, R. R. Schrock, F. J. Hollander, W. J. Youngs, and M. R. Churchill, *ibid.*, **100**, 5962 (1978); (e) E. O. Fischer and U. Schubert, *J. Organomet. Chem.*, **100**, 59 (1975); (f) E. O. Fischer, *Adv. Organomet. Chem.*, **14**, 1 (1976); (g) W. W. Greaves, R. J. Angelici, B. J. Helland, R. Klima, and R. A. Jacobson, *J. Am. Chem. Soc.* **101**, 7620 (1979); (h) E. O. Fischer, T. L. Lindner, G. Huttner, P. Friedrich, F. R. Kreisel, and G. Huttner, *Angew. Chem., Int. Ed. Engl.*, **16**, 401 (1977); (i) G. R. Clark, K. Marden, W. R. Roper, and L. J. Wright, *J. Am. Chem. Soc.*, **102**, 6570 (1980), and references therein; (j) S. J. Holmes and R. R. Schrock, *ibid.*, **103**, 4599 (1981).

(5) (a) F. N. Tebbe, G. W. Parshall, and G. S. Reddy, *J. Am. Chem. Soc.*, **100**, 3611 (1978); (b) F. N. Tebbe, G. W. Parshall, and D. W. Ovenall, *ibid.*, **101**, 5074 (1979); (c) S. H. Pine, R. Zahler, D. A. Evans, and R. H. Grubbs, *ibid.*, **102**, 3270 (1980). See also: (d) M. M. Francl and W. J. Hehre, *Organometallics*, **2**, 457 (1983).

(6) (a) L. J. Guggenberger, *Inorg. Chem.*, **12**, 294 (1973); (b) J. L. Petersen and L. F. Dahl, *J. Am. Chem. Soc.*, **97** 6416 (1975); (c) L. J. Guggenberger and R. R. Schrock, *ibid.*, **97**, 6578 (1975); (d) J. W. Lauher and R. Hoffmann, *ibid.*, **98**, 1729 (1976).

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Most structures of metal alkylidene complexes display a trigonal-planar arrangement about carbon, consistent with $sp^2$ hybridization at this center. All known carbyne complexes exhibit linear or nearly linear MCR linkages. A number of metal alkylidene complexes of the early transition metals, e.g., tantalum, have geometries that deviate considerably from normal ethylene-type structures. In particular, they exhibit large, ca. 150–180°, MCR angles and concomitantly small MCH angles, ca. 80–100°.[7] Theoretical work has shown that although steric factors may precipitate small distortions of this type, the most severe are the result of donation of the CH bonding electron pair into the metal–carbon bond, forming a new $\pi$-system perpendicular to the extant $\pi$ bond, i.e., hyperconjugation.[8] Completely saturated (18-electron) complexes would derive no benefit from such donation; it should be most important for electron-deficient systems, which are common to metals of groups 4–6.

The availability of unfilled d orbitals on the metal center has geometrical and electronic consequences beyond those associated with hyperconjugated structures. Particularly, the ability to construct more than one $\pi$-bond should result in more conformational flexibility than expected for multiply bonded systems. We report here the results of our investigations into the properties of titanium and zirconium methylidene complexes, with particular emphasis on conformational preferences, and the use of rotational barriers as a measure of $\pi$-bond strength.

## Theoretical Methods

The calculations reported in this work have been performed by using the STO-3G minimal basis set, recently extended through first- and second-row transition metals.[9] The GAUSSIAN 83 series of computer programs have been employed.[10]

There is a great deal of bias in the theoretical literature against the application of minimal basis sets such as STO-3G to the calculation of structures and energies of transition-metal systems, even though few actual comparisons have been made.[9b] While much of the criticism is well fouunded, e.g., minimal basis sets do not perform well in the calculation of orbital energies, we believe much of it is not. A systematic evaluation of the performance of such simple and widely applicable levels of theory should be made before they are discarded. A brief comparison of available experimental and higher level theoretical data for group 4 metals with data from STO-3G calculations has already been presented in an earlier paper.[8b] The results indicate a reasonable performance for STO-3G in the task of structure determination. It is likely that improved theoretical methods, including more flexible basis sets and some account of electron correlation will be necessary to accurately determine relative energetics.

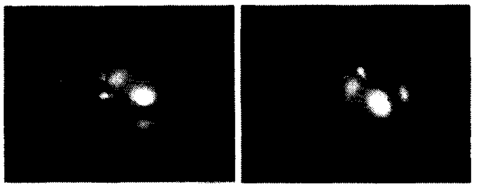


**Figure 1.** Valence $\pi$-orbitals of dihydridomethylidenetitanium (STO-3G//STO-3G): left, planar conformer; right, perpendicular conformer.

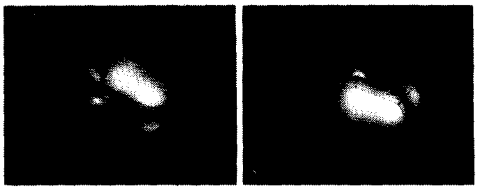
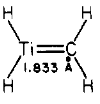


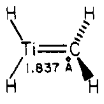
**Figure 2.** Valence $\pi$-orbitals of dihydridomethylidenezirconium (STO-3G//STO-3G): left planar conformer; right perpendicular conformer.

## Results and Discussion

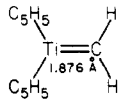
Calculated double bond lengths of "planar" and "perpendicular" conformers of dihydridomethylidenetitanium, **1**, dicyclopentadienylmethylidenetitanium, **2**, chlorohydridomethylidenetitanium, **3**, dichloromethylidenetitanium, **4**, and dihydridomethylidenezirconium, **5**, are shown. These derive from complete structure optimizations.



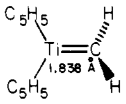
**1a**



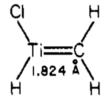
**1b**



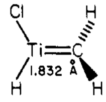
**2a**



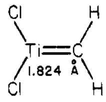
**2b**



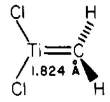
**3a**



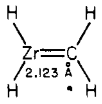
**3b**



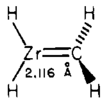
**4a**



**4b**



**5a**



**5b**

Note that twisting of the skeleton from planar to perpendicular does not result in significant lengthening of the MC double bond. The TiC linkages in **1** and **3** are lengthened by no more than 0.008 Å, while that in **4** is unchanged. Slight bond shortening is predicted for both the dicyclopentadienylmethylidenetitanium and dihydridomethylenezirconium complexes! Thus, from a standpoint of equilibrium geometry, the metal–carbon $\pi$-bond is largely unaffected by conformation.

Calculated rotation barriers, i.e., planar–perpendicular energy differences, in the eight-electron dihydrido complexes, $H_2Ti{=}CH_2$ and $H_2Zr{=}CH_2$, are 13 and 19 kcal $mol^{-1}$, respectively. Calculated barriers in the monochloro- and dichloro-substituted systems **3** and **4** are 14 and 16 kcal $mol^{-1}$, respectively. All of these barriers seem too small to accurately reflect the actual $\pi$-bond strengths in these compounds. On the other hand, the barrier hindering torsion about the double bond in the 16-electron dicyclopentadienylmethylidenetitanium complex **2** is sizable (52

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[7] (a) E. O. Fischer, G. Kreis, C. G. Kreiter, J. Müller, G. Huttner, and H. Lorenz, *Angew. Chem., Int. Ed. Engl.*, **12**, 564 (1973); (b) G. Huttner, H. Lorenz, and W. Gartzke, *ibid.*, **13**, 609 (1974); (c) L. J. Guggenberger and R. R. Schrock, *J. Am. Chem. Soc.*, **97**, 2935 (1975); (d) S. J. McLain, C. D. Wood, L. W. Messerle, R. R. Schrock, F. J. Hollander, W. J. Youngs, and M. R. Churchill, *ibid.*, **100**, 5962 (1978); (e) E. O. Fischer and U. Schubert, *J. Organomet. Chem.*, **100**, 59 (1975); (f) E. O. Fischer, *Adv. Organomet. Chem.* 14, 1 (1976); (g) W. W. Greaves, R. J. Angelici, B. J. Helland, R. Klima, and R. A. Jacobson, *J. Am. Chem. Soc.*, **101**, 7620 (1979); (h) E. O. Fischer, T. L. Lindner, G. Huttner, P. Friedrich, F. R. Kreisel, and G. Huttner, *Angew. Chem., Int. Ed. Engl.*, **16**, 401 (1977), (i) G. R. Clark, K. Marden, W. R. Roper, L. J. Wright, *J. Am. Chem. Soc.*, **102**, 6570 (1980), and references therein; (j) S. J. Holmes and R. R. Schrock, *ibid.*, **103**, 4599 (1981).

[8] (a) R. J. Goddard, R. Hoffmann, and E. D. Jemmis, *J. Am. Chem. Soc.*, **102**, 7667 (1980); (b) M. M. Francl, W. J. Pietro, R. F. Hout, Jr., and W. J. Hehre, *Organometallics*, **2**, 281 (1983).

[9] First row: (a) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969). First- and second-row transition metals: (b) W. J. Pietro and W. J. Hehre, J. *Comput. Chem.*, **4**, xxxx (1983).

[10] R. F. Hout, Jr., M. M. Francl, E. S. Blurock, W. J. Pietro, D. J. DeFrees, S. K. Pollack, B. A. Levi, R. Steckler, and W. J. Hehre, Quantum Chemistry Program Exchange, Indiana University, to be submitted for publication.

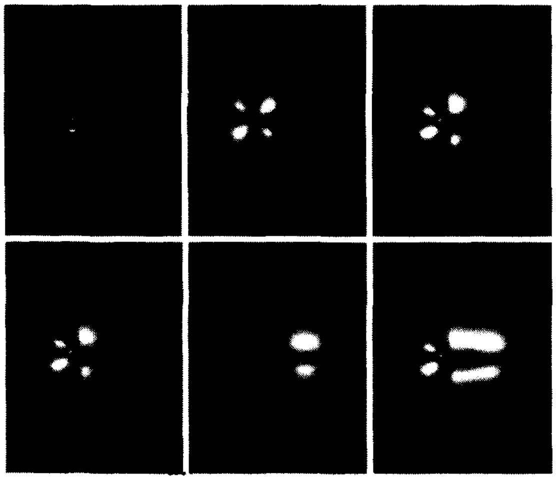
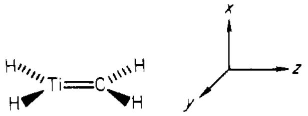


**Figure 3.** Construction of the $\pi$-bond in planar dihydridomethylidenetitanium from its component atomic orbitals. See text for discussion.

kcal mol$^{-1}$) and probably better describes the true $\pi$-bond energy. The reason for the small barriers in the highly electron-deficient (eight-electron) carbenes, and for the significant increase in barrier upon increased saturation of the metal, is easily understood with the aid of orbital photographs.[11] As shown in Figure 1, the valence $\pi$-orbitals for planar and perpendicular forms of dihydridomethylidenetitanium are virtually identical, while those for the analogous zirconium complex (Figure 2) reveal only subtle differences. Further orbital plots (Figure 3) show why. Here, construction of the $\pi$-bond in planar dihydridomethylidenetitanium from its component atomic orbitals is illustrated for the molecule oriented in the following way.



Specifically what is shown in the mixing of the $p_x$ atomic orbitals on the metal, i.e., $2p_x$, $3p_x$, $4p_x$, with the valence $3d_{xz}$ function, i.e.

$$p_x + 3d_{xz} \rightarrow p_xd_{xz}\ \text{hybrid}$$

followed by the combination of the resulting hybrid with the valence $2p_x$ on carbon to form the $\pi$-bond.

$$p_xd_{xz}(\text{metal}) + 2p_x(\text{carbon}) \rightarrow \pi\text{-bond}$$

It is important to note that it is the 3d orbital, and not inner-shell or valence p-type atomic orbitals, which makes up the major contribution of the metal to the bond. In fact, the minimal basis set calculations employed here probably overestimate the role of the 4p functions in bonding; previous theoretical work clearly suggests that the use of a split d basis set reduces the need for occupation of the high-lying p orbitals.[12] In the eight-electron complexes, the metal d orbitals are not employed to a significant extent to bind the ligands, and either or both of two components ($d_{xz}$ or $d_{yz}$) may be used to overlap with the valence 2p function on carbon to form the double bond.

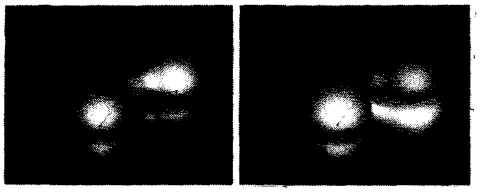


**Figure 4.** Delocalization of chlorine lone pair onto metal center in $Cl_2Ti{=}CH_2$.

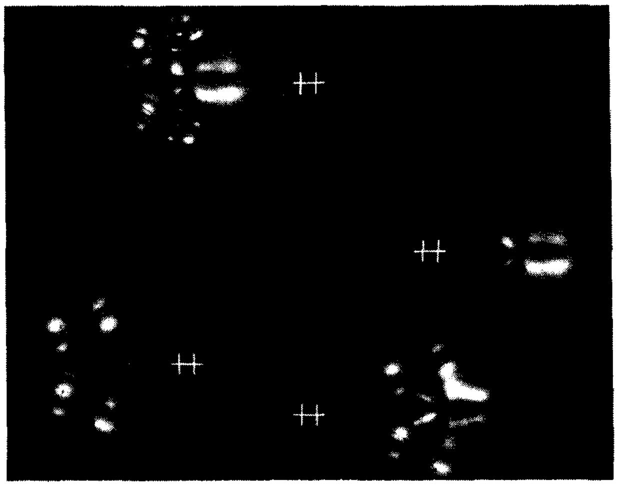


**Figure 5.** Orbital correlation diagram for dicyclopentadienyl fragment and $TiCH_2$ $\pi$-bond.

The larger barriers in the chlorine-substituted methylidene complexes are expected, since delocalization of the Cl lone pair, as illustrated in Figure 4, onto the metal partially ties up the empty d orbitals.

The origin of the much higher barrier in the 16-electron dicyclopentadienylmethylidenetitanium complex, **2**, as well as the surprising *shortening* of the TiC double bond as a result of twisting, may be rationalized in terms of the orbital correlation diagram in Figure 5. The $\pi$-bond in the planar complex does not interact significantly with the valence orbitals on the cyclopentadienyl ligands and closely resembles the analogous double bond in the eight-electron dihydrido system (left-hand side of Figure 1). On the other hand, significant mixing of metal and ligand orbitals does occur in the perpendicular geometry, giving rise to two molecular orbitals, the lower of which is metal–ligand bonding and the upper, antibonding. In net, a decrease in metal–ligand binding results, as evidenced by a increase in the average distance of the cyclopentadienyl carbons to the titanium (from 2.34 Å in the planar structure to 2.41 Å in the perpendicular). Note that both combinations are TiC $\pi$-bonding. Thus, it is not unreasonable that the linkage should shorten and not lengthen as a result of twisting. The interaction depicted in Figure 5 involves four electrons and leads to net destabilization; i.e., the upper level is raised in energy more than the lower level is reduced. Comparison of STO-3G orbital energies for planar and perpendicular forms suggests that this effect alone accounts for two-thirds of the total calculated rotation barrier. As this kind of interaction is entirely absent in the dihydrido systems, it is reasonable to expect a significant increase in rotation barrier.

Barriers to cis–trans isomerization in olefins and related main-group compounds may reasonably be expected to correlate quite closely to $\pi$-bond strengths. Twisting of the $\pi$-linkage completely destroys overlap of the valence p orbitals. The analogy does not carry over to bonds between carbon and transition metals, at least where the metal is coordinatively unsaturated, and more than a single

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[11] (a) R. F. Hout, Jr., W. J. Pietro and W. J. Hehre, *J. Comput. Chem.*, 4, xxxx (1983). (b) R. F. Hout, Jr., W. J. Pietro, and W. J. Hehre, "A Pictorial Guide to Molecular Structure and Reactivity", Wiley, New York, in press. (c) R. F. Hout, Jr., W. J. Pietro, and W. J. Hehre, Quantum Chemistry Program Exchange, Indiana University, to be submitted for publication.

[12] See, for example: J. A. Connor, I. H. Hillier, V. R. Saunders, M. H. Wood, and M. Barber, *Mol. Phys.*, 24 , 497 (1972).

d orbital is available for bonding. Even for coordinatively saturated compounds, the validity of such an hypothesis must seriously be questioned. Thus, the existing data from NMR spectroscopy on rotational barriers in metal carbenes, while interesting, do not necessarily provide information on the $\pi$-bond strengths in these compounds. Alternative criteria need to be adopted.

Calculated Mulliken $\pi$-overlap populations[13] for planar dihydridomethylidenetitanium, **1a**, and dihydridomethylidenezirconium, **5a**, are of comparable magnitude to that in isobutene and significantly larger than values for main-group isobutene analogues, i.e., 1,1-dimethylsilaethylene, 1,1-dimethylgermaethylene, and 1,1-dimethylstannaethylene.[14] This suggests that the $\pi$-bond strengths in both the eight-electron titanium and zirconium methylidene complexes may be comparable to those in normal olefins, e.g., 65 kcal mol$^{-1}$ in ethylene,[15] and considerably larger than those in the main-group olefin analogues, ca., 30–45 kcal mol$^{-1}$.[16] Increased coordination of the metal leads to a marked decrease in $\pi$-overlap population and presumably to a decrease in $\pi$-bond strength.

The present results are qualitative and must await better theoretical treatments and/or experimental thermochemical measurements. Both are in progress in our laboratory. They do suggest, however, that $\pi$-bonds between carbon and transition metals are likely to be much stronger than those in analogous main-group compounds. This is entirely consistent with the multitude and diversity of known transition-metal carbenes, compared to the scarcity of stable compounds incorporating double bonds between carbon and heavier main-group elements.

**Registry No.** **1a**, 78499-81-7; **2a**, 85028-89-3; **3a**, 85028-90-6; **4a**, 79899-81-3; **5a**, 85028-91-7.

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[13] R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841, 2338, 2343 (1955).

[14] W. J. Pietro, M. M. Francl and W. J. Hehre, unpublished calculations.

[15] J. E. Douglas, B. S. Rabinovitch, and F. S. Looney, *J. Chem. Phys.*, **23**, 315 (1955).

[16] W. J. Pietro and W. J. Hehre, *J. Am. Chem. Soc.*, **104**, 4329 (1982), and references therein.

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# Phosphorus- and Arsenic-Bridged [1]Ferrocenophanes. 3. Hydroformylation Catalyzed by the Products of the Interaction of $Co_2(CO)_8$ with 1,1′-Ferrocenylenephenylphosphine Oligomers and Polymers

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Reactions of $Co_2(CO)_8$ with ferrocenylphosphine oligomers of the type $H[-(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4PPh)-]_xPh$ (I, $x$ = 1–4) and $Ph_2P[-(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4PPh)-]_xPh$ (III, $x$ = 1, 2) or polymers of the type $H[-(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4PPh)-]_xOH$ (II, $\bar{M}_w$ 8900–161 000 amu) have been studied. Detailed IR and $^{31}P$ NMR spectroscopic investigations revealed that the polymeric ligands chelate Co in a tridentate fashion, similar to I ($x$ = 3), when a high P/Co ratio is used. Use of such Co catalysts at 170–190 °C for the hydroformylation of 1-hexene revealed reactivity and selectivity similar to those of $PPh_3$ for ligands of type I and type III, while Co complexes of the polymers, II, demonstrated a $\bar{M}_w$-dependent activity and a lower selectivity to alcohols. It is felt that the observed tendency for tridentate chelation in these complexes inhibits the aldehyde-to-alcohol reduction step. A $^{31}P$ NMR study of the cobalt complex of the trimer I ($x$ = 3) provided evidence for the presence of two enantiomeric isomers and selective quadrupolar broadening in the equatorial direction.

## Introduction

We have recently reported[1] that the reaction of (1,1′-ferrocenediyl)phenylphosphine with 1 molar equivalent of 1-lithio-1′-(diphenylphosphino)ferrocene in THF resulted in the formation of oligomers. After hydrolysis, species of type I were obtained ($x$ = 1–5) which were separated by preparative-scale high-performance liquid chromatography. In a similar fashion, reaction of 1 or 2 molar equivalents of 1-lithio-1′-(diphenylphosphino)ferrocene with two of diphenylchlorophosphine or one of phenyldichlorophosphine resulted in the isolation of symmetrical dimer III ($x$ = 1) or trimer III ($x$ = 2), respectively. Under appropriate conditions (temperature, mode of addition, solvent), the reaction of 1,1′-dilithioferrocene tetra-

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[1] Withers, H. P.; Seyferth, D.; Fellmann, J. D.; Garrou, P. E.; Martin, S. *Organometallics* 1982, *1*, 1283.