Table I. ^{1}H NMR[a] and IR[b] Data

compd	^{1}H NMR, ppm	IR ν(CO), cm^{-1}
Ia	2.36 (s)	1968, 1920[c]
Ib	2.25 (s)	1971, 1921[c]
Ic	2.25 (s)	1972, 1920[c]
Id	2.43 (s) [9 H],[d] 5.1 (s) [3 H]	1981, 1973[e]
II	2.35 (s) [18 H], −10.9 (s) [1 H][e]	1945, 1890[e]

[a] In $CDCl_3$. [b] All absorption bands are strong. [c] Acetone. [d] Relative number of protons. [e] Dichloromethane.

analogues, the carbonyl stretching frequencies of compounds Ia–d are lower than their corresponding tricarbonyl cations. The ^{1}H NMR spectra for compounds Ia–c (Table I) all consist of a singlet between 2.25 and 2.36 ppm. Compound Id shows two singlets as expected for coordinated mesitylene (MES) with the aromatic ring protons shifted upfield by 1.60 ppm relative to uncoordinated mesitylene.[12] The proton-decoupled ^{13}C NMR spectrum of Ia reveals three singlets: 228.6 (Mn–CO), 104.0 (Mn–*C*–C), and 16.75 ppm (Mn–C–*C*). The nondecoupled spectrum shows the resonance at 16.75 ppm splits into a quartet as expected for the proposed structure. Mass spectral data for Ia show a parent ion at *m/z* 400 and ions at *m/z* 344 and 217 as expected for the parent minus two carbonyls and the parent minus two carbonyls and an iodide, respectively. The mass spectra of Ib and Ic show no parent ions but display ions consistent with decomposition pathways predicted for compounds I.[10]

Compound II, a yellow solid, was synthesized from Ia in THF, at 50 °C, with an excess of $NaBH_4$ (eq 2). The

$$\mathrm{Ia} + \mathrm{NaBH_4} \rightarrow \underset{\mathrm{II}}{(\mathrm{HMB})\mathrm{Mn(CO)_2H}} \qquad (2)$$

reduction required 2–5 h and was monitored by change in the CO stretching frequency of the IR spectrum. It was isolated by vacuum sublimation from the solid residue left by vacuum evaporation of the solvent. This new compound, to our knowledge, the first reported isolable (η^6-arene)metal carbonyl hydride, has been characterized by mass, ^{1}H NMR, and IR spectroscopy and elemental analysis (Table I, ref 10 and 11). The chemical shift of the Mn–*H*, (CH_2Cl_2) −10.9 ppm, is comparable to that of $(\eta^5\text{-}C_5(CH_3)_5)Fe(CO)_2H$[13] and is characteristic of transition-metal hydrides. Like compounds I, when heated, II undergoes a transition from 120 to 130 °C with loss of a white crystalline solid that melts at 163 °C. The lack of bimolecular elimination of H_2 from II up to 120 °C is consistent with the behavior of $(\eta^5\text{-}C_5(CH_3)_5)Fe(CO)_2H$, which is reported to be thermally stable.[14] In contrast to the instability of $CpFe(CO)_2H$,[15] which decomposes giving H_2 at 20 °C, the stability of both of these compounds may be due to the steric hindrance of bimolecular interaction accompanying permethylation of the π ligands.

Compound Ib reacts with NaCN in refluxing methanol to yield, quantitatively by IR, η^6-ArMn(CO)$_2$CN, III (eq 3).[16] The melting point, IR, and ^{1}H NMR all agree with

$$\mathrm{Ib} + \mathrm{NaCN} \rightarrow \underset{\mathrm{III}}{(\mathrm{HMB})\mathrm{Mn(CO)_2CN}} \qquad (3)$$

literature values.[1] Ib also reacts with MeLi, at −78 °C in THF, to quantitatively yield the previously reported η^6-ArMn(CO)$_2$Me, IV (eq 4).[16] The spectroscopic charac-

$$\mathrm{Ib} + \mathrm{MeLi} \rightarrow \underset{\mathrm{IV}}{(\mathrm{HMB})\mathrm{Mn(CO)_2Me}} \qquad (4)$$

teristics (IR and NMR) match the literature reported values.[2] The three reactions summarized in eq 2–4 show the synthetic utility of compounds I with respect to nucleophilic displacement of the halide. This reactivity corresponds directly to that displayed by the isoelectronic $CpFe(CO)_2X$ analogues.[17]

We are currently in the process of exploring the synthetic utility of this new series of halides as well as the hydride. In addition an X-ray crystallographic study of Ic is in progress.

Registry No. Ia, 91230-49-8; Ib, 91230-50-1; Ic, 91230-51-2; Id, 91230-52-3; II, 91230-53-4; III, 41638-97-5; IV, 65643-58-5; (HBM)Mn(CO)$_3^+$AlCl$_3$Br$^-$, 91230-54-5; (MES)Mn(CO)$_3^+$AlCl$_3$Br$^-$, 91238-35-6.

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(11) Anal. Calcd for Ia: C, 42.02; H, 4.53. Found: C, 41.45; H, 4.54. Anal. Calcd for Ib: C, 47.62; H, 5.14. Found: C, 47.24; H, 5.06. Anal. Calcd for Ic: C, 54.47; H, 5.88. Found: C, 54.05; H, 5.61. Anal. Calcd for II: C, 61.32; H, 6.99. Found: C, 61.23; H, 7.11.

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Diastereomeric Equilibria and Barrier of Rotation in Cationic Iron Diphosphine Alkylidenecarbene (Vinylidene) Complexes

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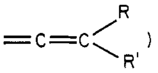
Summary: In the preferred geometry for $[(\eta\text{-}C_5H_5)Fe(\text{diphosphine})(C{=}CHR)]PF_6$ complexes the plane of the alkylidenecarbene ligand is not perpendicular to that of the cyclopentadienyl ligand; barriers for rotation have been evaluated to be 9–10 kcal/mol through ^{31}P NMR spectroscopy. The equilibrium composition of the two diastereomeric conformers for complexes containing the 2,3-butanediylbis(diphenylphosphine) ligand is influenced by the bulkiness of the substituent on the alkylidenecarbene moiety (C_6H_5 vs. CH_3); when *trans*-1,2-cyclopentanediylbis(diphenylphosphine) is the ligand, only one rotamer is recognizable in the low-temperature spectra for R = methyl, *tert*-butyl, and phenyl.

Table I. Some NMR Parameters and Diastereomeric Composition for $[(\eta\text{-}C_5H_5)Fe(L\text{-}L)(C{=}CHR)]PF_6$ Complexes[a]

complex	L-L	C=CHR R =	T, K	$\delta(C_5H_5)$	$\delta(P_A)$	$\delta(P_B)$	$J_{P\text{-}P}$, Hz	$\delta(=C)$	$^2J_{C\text{-}P}$, Hz	dc,[b] %
1	diphos	C_6H_5	298	5.23	93.5			365	35	
			180	nd	97.4	91.4	42	366	33	
2a	(*S*,*S*)-chiraphos	C_6H_5	298	5.01	94.8	93.2	52	355	29, 35	
			168	nd	103.2	92.1	48	nd	nd	86
				nd	84.0	93.7	60	nd	nd	14
2b	(*S*,*S*)-chiraphos	CH_3	289	4.86[c]	100.9	96.1	50	359	26, ~0	
			153	nd	~105	96.6	nd[d]	nd	nd	55
				nd	~105	95.2	nd[d]	nd	nd	45
3a	*trans*-cypenphos	C_6H_5	298	5.00	71.5	69.0	61	367	29, 37	
			173	nd	71.4	72.9	61	nd	nd	>90
3b	*trans*-cypenphos	CH_3	289	4.86[c]	74.6	72.1	61	362	28, 37	
			152	nd	74.6	75.7	62	nd	nd	>90
3c	*trans*-cypenphos	$t\text{-}C_4H_9$	298	4.78	73.8	68.2	60	364	28, 36	
			168	nd	74.8	71.6	60	nd	nd	>90

[a] The spectra were obtained from either a Bruker AM 300 WB or a Bruker WP 200 using mixtures $CD_2Cl_2/CDCl_3$ (70–30) as the solvent for ^{31}P and ^{13}C spectra and $CDCl_3$ (unless otherwise stated) for ^1H spectra. [b] dc = diastereomeric composition. [c] At 298 K in CD_2Cl_2. [d] The coupling constant cannot be exactly given because of the incomplete resolution of these two doublets. nd = not determined.

Transition-metal alkylidenecarbene (vinylidene) complexes have been the subject of much recent interest.[1,2] Stereochemical studies on such complexes, however, are still rare.[3] Since the substituted alkylidenecarbene ligand



$(=C=C(R)(R'))$

is a two-dimensional chiral simplex,[4] it forms a chiral unit when bound to a metal in a complex that does not have a symmetry plane which would contain that ligand. Diastereomers will therefore arise, if in the complex another chirality element is present. This has been indeed recognized in pseudotetrahedral rhenium complexes in which the rhenium atom is a chirality center.[3] No example of diastereomeric equilibria for complexes having chiral ligands has been reported as far as we are aware. Such type of investigation can contribute to a better understanding of the basic phenomena in homogeneous asymmetric catalysis.[5]

We report some results of the investigation of diastereomeric equilibria in complexes of the type $[(\eta\text{-}C_5H_5)Fe(C{=}CHR)(L\text{-}L)]PF_6$ (Figure 1), where L-L is a C_2 diphosphine, namely, (2*S*,3*S*)-2,3-butanediylbis(diphenylphosphine) (chiraphos)[6] or racemic *trans*-1,2-cyclopentanediylbis(diphenylphosphine)[7] (*trans*-cypenphos) and R = C_6H_5, $t\text{-}C_4H_9$, and CH_3 by using ^{31}P NMR spectroscopy. Also the $[(\eta\text{-}C_5H_5)Fe(C{=}CHPh)(diphos)]PF_6$ complex (where diphos is 1,2-ethanediylbis(diphenylphosphine)) (Figure 1) has been investigated, in order to identify the preferred geometry of the vinylidene ligands within the complexes in solution.

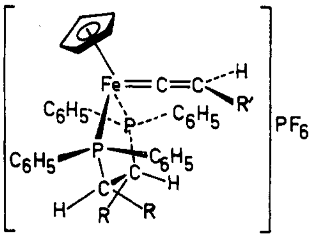


Figure 1. 1, (R = H, R′ = C_6H_5; **2a**, R = CH_3, R′ = C_6H_5; **2b**, R = R′ = CH_3; **3a**, R, R = $-(CH_2)_3-$, R′ = C_6H_5; **3b**, R, R = $-(CH_2)_3-$, R′ = CH_3; **3c**, R, R = $-(CH_2)_3-$, R′ = $t\text{-}C_4H_9$.

In spite of the high endothermicity of the transformation alkyne–alkylidenecarbene,[8] the compounds form smoothly (reaction time less than 1 h at room temperature) when $(\eta\text{-}C_5H_5)Fe(L\text{-}L)Br$ complexes (obtained according to literature procedures[9,10]) are treated[11,12] with monosubstituted acetylenes in methanol in the presence of KPF_6 or NH_4PF_6 as the halogen scavenger.[13] The nature of the complexes is inferred by the presence in the ^{13}C NMR spectrum of a resonance at 355–365 ppm[1,3,11,14] (Table I) and by ν(C=C) bands in their IR spectra[1] between 1620 and 1670 cm^{-1}.

For the similar $[(\eta\text{-}C_5H_5)Ru(C{=}CHMe)(PMe_3)_2]PF_6$ complex, it has been found[15] that the plane of the ethylidenecarbene ligand bisects the molecular symmetry plane in the solid state (this corresponds to the geometry reported in Figure 1). However, recent SCF calculations for iron complexes imply similar total orbital energies for that conformation and for the one in which the plane of the alkylidenecarbene ligand coincides with the molecular symmetry plane.[16]

Variable-temperature ^{31}P NMR spectroscopy on 1 (Figure 1 and Table I) allows us to identify the preferred geometry for that ligand. As a matter of fact, the single line observable in the spectrum at room temperature gives rise to an AB quartet at low temperature (Table I), the coalescence temperature being 210 K. If we reasonably assume (vide infra) that λ–δ equilibration of the chelation ring is still rapid at the temperature of the limiting spec-

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(13) Correct elemental analyses have been obtained for all of the reported complexes, e.g., **2b** and **3b**. Calcd for $C_{36}H_{37}F_6FeP_3$ (**2b**): C, 59.04; H, 5.09. Found: C, 58.52; H, 5.02. Calcd for $C_{37}H_{37}F_6FeP_3$ (**3b**): C, 59.69; H, 5.01. Found: C, 58.67; H, 5.11.

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trum, an AB quartet for the two phosphorus atoms can only arise from the geometry reported in Figure 1 (some distortion from that idealized geometry appears possible). For this geometry the two phosphorus atoms are diastereotopic[17] and the two rotamers are enantiomers. In the alternative geometry the two phosphorus atoms would be enantiotopic[17] and the two rotamers would be diastereomers (a two-line spectrum is in principle expected). This latter geometry was proposed for the carbene complex $[(\eta\text{-}C_5H_5)Fe(diphos)({=}CH_2)]^{+}$[18] and accords with the geometry of the alkylidenecarbene complexes on the basis of the fact that in metallocumulenes complexes neighboring homologues have orthogonal carbon π termini.[3]

It is to remark that the line at 298 K does not exactly coincide with the baricenter of the AB quartet observed at low temperature (Table I). This may be attributed to a simple temperature-dependent solvent effect, to a shift of the equilibrium betwen λ and δ diastereomeric conformations of the chelation ring, and/or even to some conformational adjustment of the benzylidenecarbene ligand. If that implies (as it appears possible) a variation of the chemical shift difference of the phosphorus resonances, the line shape analysis ($\Delta H^{\ddagger} = 10.2 \pm 0.2$ kcal/mol, $\Delta S^{\ddagger} = 2.7 \pm 0.9$ eu) gives only a rough extimate of the energetics of the process. The energy barrier for rotation estimated from the coalescence temperature[19] is ~9.4 kcal/mol.

A similar investigation on the corresponding (*S*,*S*)-chiraphos containing complexes **2** (Figure 1 and Table I) reveals the same type of nonrigid behavior. For these complexes no significant population for the conformer having the λ conformation of the five-membered chelate ring is expected.[6] For complex **2a** the pair of doublets present in the spectrum at room temperature gives rise to two pair, of doublets of relative intensities 86:14 at 168 K. Coalescence of P_A (Table I) takes place at a temperature (~220 K) higher than that of P_B (~205 K), as expected,[20] allowing us to evaluate an energy barrier for rotation of ~9.7 kcal/mol for the prevailing rotamer, the difference in free energy of formation for the two diastereomeric rotamers being ~0.55 kcal/mol. Diastereomeric equilibrium is ~55:45 for complex **2b** at 153 K; the energy barrier for rotation seems somewhat lower than that of **2a**. The signal corresponding to P_B (Table I) decoalesces at ~180 K and splits into two doublets, which are still not completely resolved at 153 K. At this temperature the signal of P_A, which has considerably shifted downfield, has broadened but still not split.

For the complexes **3**, which contain the *trans*-cypenphos ligand, only one set of signals is evident in the low-temperature spectra (Table I). This may be attributed to a larger prevalence of one conformation of the alkylidenecarbene ligand or to a substantially smaller rotational barrier than in complexes **1** and **2**; the latter explanation appears much less probable. In fact for these three complexes by lowering the temperature the downfield signal due to the phosphorus atom labeled P_A in Table I retains more or less its chemical shift. By contrast, the signal corresponding to the other phosphorus atom (P_B) (which is broader than that of P_A at higher temperature) shifts downfield. For the complexes **3a** and **3b** this shift causes the upfield signal to become downfield at low temperature; the phosphorus atoms appear isocronous at 233 K for **3a** and at 210 K for **3b**. The signals retain always the coupling with each other. A comparison with the behavior of complexes **2** suggests that this shift is caused by the decreasing of the concentration below the detection limits of the less stable rotamer as a consequence of the decreasing temperature.

Studies are in progress on similar ruthenium complexes also containing analogous C_1 chiral diphosphine ligands;[21] they reveal the optical stability at the metal atom and should eventually cast more light on the influence of the chirality at the metal (in addition to that of the chiral ligand) on the reported phenomena of asymmetric discrimination. Such chirality at the metal can indeed play a very important role on asymmetric transformations involving prochiral organic ligands bound to chiral transition-metal complexes.[22]

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