

Structural and Electronic Effects in (Benzylideneacetone)dicarbonyl(phosphine)iron(0) and (Benzylideneacetone)dicarbonyl(phosphite)iron(0) Complexes. A Carbon-13 Magnetic Resonance Study

EDUARDO J. S. VICHI,* FRED Y. FUJIWARA, and EDISON STEIN

Received September 15, 1983

The structures in solution and the electronic effects induced by the ligands L in the series (benzylideneacetone)Fe(CO)₂L (L = CO, tertiary phosphines, and tertiary phosphites) were studied by ¹³C NMR spectroscopy. In contrast to the tricarbonyl derivative, which is fluxional at 32 °C, the compounds containing a phosphorus ligand do not show fluxional behavior at this temperature. This could be attributed to an increase in the π back-donation from the filled metal d orbitals to the LUMO of benzylideneacetone (BDA) induced by the better σ-donor and poorer π-acceptor phosphorus ligands, compared to CO. The resonances of coordinated BDA show a very large upfield shift at the carbons directly involved in bonding with iron. The differences in the chemical shifts at the terminal carbon of the heterodiene function in coordinated and free BDA, ΔC₄, correlate reasonably well with the basicities of the phosphorus ligands while the ratio ΔC₄/ΔC₃ correlates with the Tolman electronic parameter, ν, of the phosphorus ligands. The results are interpreted on the basis of a bonding model in which the coordinated BDA acts as a "sink" for the negative charge placed in the iron atom by the phosphorus ligand via a P → Fe ← BDA mechanism.

Introduction

The structure of transition-metal complexes containing diene, carbonyl, and phosphorus ligands and the transmission of electronic effects in these complexes are related to the nature of both metal–diene and metal–phosphorus bonds.¹ There is agreement that the metal–diene bonding involves donation of electrons from the highest occupied molecular orbital (HOMO) of the diene to vacant metal d orbitals (or hybrid orbitals) and back-donation from a filled metal orbital into the diene lowest unoccupied molecular orbitals (LUMO).²⁻⁵ Concerning the metal–phosphorus bonds, transition-metal chemistry abounds with discussions of the relative contributions of σ and π bonding.⁶⁻⁸ It appears that the phosphorus ligands cannot be characterized by definite donor–acceptor capacities, as these capacities are also dependent on the overall electron density of the complex to which they are bonded.

The available X-ray data for (diene)Fe(CO)₃⁹ and (cyclohexene)Fe(CO)₂PPh₃¹⁰ complexes suggest that the geometry adopted in the solid state is something between a tetragonal pyramid and a pseudooctahedron. In solution, the departure from five-coordination and the mixing of "six-coordinated character" are associated with the reluctance of the (η-diene)Fe(CO)₃ to undergo isomerization and rearrangements by unimolecular processes.¹¹ The activation barrier for carbonyl scrambling in complexes of 1,3-diene increases with the acceptor abilities of the diene and donor abilities of the metal carbonyl fragment.¹¹ The intramolecular CO exchanges in several (diene)iron tricarbonyls with heteroatoms in the 1- and/or 4-position of the diene¹² were found to have higher barriers than those observed with less polar dienes.

In a previous paper¹³ we presented the X-ray structure of the complexes (BDA)Fe(CO)₂L (BDA = benzylideneacetone; L =

triphenylphosphine and dimethylphenylphosphine). It was shown that the iron atom adopts a distorted octahedral geometry in which three facial sites are occupied by the BDA ligand. The two carbonyl groups are cis to each other while the phosphine is approximately trans to the midpoint of the central C–C bond of the heterodiene function. However, X-ray diffraction is a rather limited technique to reliably determine small electronic effects arising from perturbations of the molecular orbitals.¹⁴

In this paper we discuss the results obtained in a ¹³C NMR study of (BDA)Fe(CO)₂L (L = CO, phosphine, phosphite) complexes, in an attempt to detect and interpret such electronic perturbations.

Experimental Section

(BDA)Fe(CO)₂L (L = CO,¹⁵ P(OPh)₃,¹⁶ PPh₃,¹⁶ PEt₃,¹³ PPh₂Me,¹³ and PPhMe₂¹³) compounds were prepared and purified according to published procedures. The new complexes (BDA)Fe(CO)₂L with L = PCy₃ and P(o-tol)₃ were prepared by the photolytic method described in ref 13 and 16, and those with L = P(OMe)₃ and P(OEt)₃ as described in ref 16.

(Benzylideneacetone)dicarbonyl(tricyclohexylphosphine)iron(0) and (Benzylideneacetone)dicarbonyl(tri-*o*-tolylphosphine)iron(0). Tricyclohexylphosphine (2.8 mmol; 790 mg) or tri-*o*-tolylphosphine (2.8 mmol; 850 mg) were dissolved in tetrahydrofuran (THF) (100 mL). Dodecacarbonyliron (0.94 mmol; 470 mg) was added and the solution stirred at 70 °C until the green color had disappeared completely (ca. 1 h). The resulting solutions were filtered after cooling, and the solvent was removed under vacuum to give solid Fe(CO)₄PCy₃ (dark red; ν_{C=O} (cyclohexane) 2005, 1967, 1927 cm⁻¹) or solid Fe(CO)₄P(o-tol)₃ (brown; ν_{C=O} (cyclohexane) 2040, 1970, 1940 cm⁻¹). Fe(CO)₄PCy₃ (500 mg; 1.12 mmol) or Fe(CO)₄P(o-tol)₃ (520 mg; 1.10 mmol) was dissolved in benzene (200 mL), and after the addition of benzylideneacetone (1.48 mg; 1.10 mmol) the solution was irradiated for 24 h. The resulting red-brown solutions were filtered, and the solvent was removed under vacuum. The residues were chromatographed on silica gel. Elution with benzene gave some unreacted Fe(CO)₄PCy₃ or Fe(CO)₄P(o-tol)₃ and a second elution with 10% ethyl acetate–benzene gave, after recrystallization from *n*-pentane, the following products, respectively.

(BDA)Fe(CO)₂PCy₃: orange-red crystals; 180 mg (33% yield based on BDA); mp 152.5–153.5 °C. Anal. Calcd for C₃₀H₄₃FeO₃P: C, 66.9; H, 8.1; P, 5.8. Found: C, 67.7; H, 8.0; P, 5.7. ¹H NMR: δ 2.36, d, J_{PH} = 2.5 Hz (C(1)H₃); δ 2.56, t, J_{HH} = J_{PH} = 8.5 Hz (C(4)H); δ 5.41, dd, J_{HH} = 8.5 Hz, J_{PH} = 2.0 Hz (C(3)H). IR: ν_{C=O} (cyclohexane) 1985, 1923 cm⁻¹.

(BDA)Fe(CO)₂P(o-tol)₃ (red-brown crystals; 90 mg (16% yield based on BDA); mp 128–129 °C. Anal. Calcd for C₃₃H₃₁FeO₃P: C, 70.5; H, 5.6; P, 5.5. Found: C, 68.8; H, 5.7; P, 5.6. ¹H NMR: δ 2.37, d, J_{PH}

- Malatesta, L.; Cenini, S. "Zerovalent Compounds of Metals"; Academic Press: London, 1974.
- Churchill, M. R.; Mason, R. *Adv. Organomet. Chem.* **1967**, *5*, 93–135.
- Connor, J. A.; Derrick, L. M. R.; Hall, M. B.; Hillier, I. H.; Guest, M. R.; Higginson, B. R.; Lloid, D. R. *Mol. Phys.* **1974**, *28*, 1193–1196.
- Elián, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058–1076.
- Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **1977**, 20–37.
- (a) Cotton, F. A.; Krahenzel, C. S. *J. Am. Chem. Soc.* **1962**, *84*, 4432–4438. (b) Cotton, F. A. *Inorg. Chem.* **1964**, *3*, 702–711. (c) Graham, W. A. G. *Inorg. Chem.* **1968**, *7*, 315–321.
- Bigorgne, M. J. *Inorg. Nucl. Chem.* **1964**, *26*, 107–115; *J. Organomet. Chem.* **1964**, *2*, 101–119.
- Angelici, R. J.; Malone, M. D. *Inorg. Chem.* **1967**, *6*, 1731–1736.
- Kruger, C.; Barnett, B. L.; Brauer, O. "The Organic Chemistry of Iron"; Koerner von Gustorf, E. A., Grevels, F. W., Fischler, I., Eds.; Academic Press: New York, 1978; Chapter 1 and references therein.
- Pearson, A. J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1981**, 884–891.
- Kruczynski, L.; Takats, J. *Inorg. Chem.* **1976**, *15*, 3140–3147.
- Leibfritz, D.; tom Dieck, H. *J. Organomet. Chem.* **1976**, *105*, 255–261.
- Vichi, E. J. S.; Raithby, P. R.; Mc Partlin, M. *J. Organomet. Chem.* **1983**, *256*, 111–124.

- Coates, G. E.; Green, M. L. H.; Wade, K. "Organometallic Compounds", 3rd ed.; Chapman and Hall: London, 1972; Vol. 2.
- Howell, J. A. S.; Johnson, B. F. G.; Josty, P. L.; Lewis, J. J. *Organomet. Chem.* **1972**, *39*, 329–333.
- Johnson, B. F. G.; Lewis, J.; Stephenson, G. R.; Vichi, E. J. S. *J. Chem. Soc., Dalton Trans.* **1978**, 369–373.

= 2.7 Hz (C(1)H₃); δ 2.28, t, $J_{\text{HH}} = J_{\text{PH}} = 8.5$ Hz (C(4)H); δ 5.56, dd, $J_{\text{HH}} = 8.5$ Hz, $J_{\text{PH}} = 2.0$ Hz (C(3)H). IR: $\nu_{\text{C=O}}$ (cyclohexane) 2000, 1940 cm⁻¹.

(Benzylideneacetone)dicarbonyl(trimethyl phosphite)iron(0) and (Benzylideneacetone)dicarbonyl(triethyl phosphite)iron(0). Trimethyl phosphite (2.0 mmol; 248 mg) or triethyl phosphite (2.0 mmol; 330 mg) and (benzylideneacetone)tricarbonyliron(0) (2.0 mmol; 571 mg) were dissolved in benzene (60 mL), and the solution was heated under reflux until the $\nu_{\text{C=O}}$ bands of the starting materials had vanished from the infrared spectra of the reacting mixtures. The solvent was removed under vacuum, and the resulting material was chromatographed in silica gel. Elution with 10% ethyl ether–petroleum ether (40–60 °C) gave orange oils, which gave, after recrystallization, the following products, respectively.

(BDA)Fe(CO)₂P(OMe)₃: orange-red crystals; 190 mg (25% yield), mp 41.0–41.5 °C. Anal. Calcd for C₁₅H₁₉FeO₆P: C, 47.1; H, 5.0; P, 8.1. Found: C, 47.8; H, 5.3; P, 8.1. ¹H NMR: δ 2.30, d, $J_{\text{PH}} = 4.0$ Hz (C(1)H₃); δ 2.90, t, $J_{\text{HH}} = J_{\text{PH}} = 8.5$ Hz (C(3)H); δ 5.56, dd, $J_{\text{HH}} = 8.5$ Hz, $J_{\text{PH}} = 2.5$ Hz (C(4)H). IR: $\nu_{\text{C=O}}$ (cyclohexane) 2000, 1940 cm⁻¹.

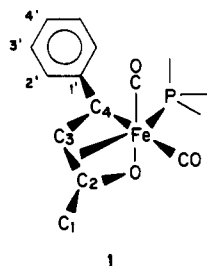
(BDA)Fe(CO)₂P(OEt)₃: orange-red crystals; 310 mg (37% yield); mp 32–34 °C. Anal. Calcd for C₁₈H₂₃FeO₆P: C, 51.0; H, 6.0; P, 7.3. Found: C, 51.9; H, 6.0; P, 7.6. ¹H NMR: δ 2.33, d, $J_{\text{PH}} = 4.0$ Hz (C(1)H₃); δ 2.89, t, $J_{\text{HH}} = J_{\text{PH}} = 8.5$ Hz (C(4)H); δ 5.55, dd, $J_{\text{HH}} = J_{\text{PH}} = 2.5$ Hz. IR: $\nu_{\text{C=O}}$ (cyclohexane) 2000, 1945 cm⁻¹.

The photolyses were carried out under a dry nitrogen atmosphere in a quartz annular reactor by using a 125-W medium-pressure mercury lamp; ¹H NMR spectra were obtained in benzene solutions on a Varian Associates XL-100 spectrometer, and IR spectra on a Perkin-Elmer 399B spectrometer. Carbon and hydrogen analyses were carried out at the Research Center of Rhodia in Campinas, and phosphorus was determined in our laboratory by a standard method.¹⁷

The ¹³C NMR spectra were obtained on saturated or nearly saturated solutions of C₆D₆ or CDCl₃ in capillary tubes of 1.7-mm diameter with a Varian XL-100 spectrometer operating at 25.2 MHz. The spectra were obtained by using a tilt angle of 25°, a repetition time of 1.7 s and a sweep width of 6151 Hz. Normally 10–15 h of accumulation was sufficient. Under these conditions, the carbonyl groups are partially saturated and tris(2,4-pentanedionato)chromium(III), Cr(acac)₃, was added to some of the solutions to increase the relaxation rate. With the concentration used, [substrate]:[Cr(acac)₃] = 100:1, negligible effects on the chemical shifts and line widths were observed. The ¹³C NMR spectra of (BDA)Fe(CO)₃ were obtained in 10- and 12-mm sample tubes in order to observe the exchange-broadened carbonyl resonances at ambient temperature and to reduce the accumulation time for the low-temperature spectra. The temperature was measured with use of a copper–constantan thermocouple. Solvent resonances were normally used as secondary standards and converted to the Me₄Si scale with the relations $\delta_{\text{Me}_4\text{Si}} = 128.0 + \delta_{\text{C}_6\text{D}_6}$ and $\delta_{\text{Me}_4\text{Si}} = 76.9 + \delta_{\text{CDCl}_3}$.

Results

The structure of the (BDA)Fe(CO)₂L complexes as well as the numbering scheme used to identify the carbons is represented by 1. The ¹³C NMR data for the complexes studied in this work



are shown in Table I. The complexes (BDA)Fe(CO)₂L (L = phosphine or phosphite) do not exhibit fluxional behavior in the ¹³C NMR spectra or more than one geometric isomer at 32 °C. The complex (BDA)Fe(CO)₃ is fluxional at 32 °C, but the line width of the averaged resonance (line width at half-height ca. 100 Hz) indicates that this temperature is only slightly above the coalescence temperature. The spectrum of (BDA)Fe(CO)₃ at -39 °C shows three resonances with no detectable line broadening due to exchange processes.

The assignments of C3 and C4 resonances were based on the single-frequency off-resonance decoupled spectrum of (BDA)-

Fe(CO)₂PEt₃. In the ¹H NMR spectrum, the multiplets at δ 5.39 ($J_{\text{PH}} = 2$ Hz, $J_{\text{HH}} = 8.5$ Hz) and δ 2.26 ($J_{\text{PH}} = J_{\text{HH}} = 8.5$ Hz) can be assigned to the protons at C3 and C4, respectively, on the basis of the characteristic large high-field shift of the “terminal” protons of iron–diene complexes.^{13,15,16} The partially decoupled ¹³C spectrum shows that the high-field olefinic carbon is coupled to the high-field olefinic proton. From the decoupled and partially coupled spectra, it was not possible to assign the two resonances of the carbons without attached protons, the carbonyl carbon (C2) and the aromatic carbon (C1') of BDA. However these two carbons can be readily assigned by comparison with the spectrum of the (cinnamaldehyde)Fe(CO)₃ complex¹² since cinnamaldehyde has the same structure as BDA but lacks the methyl group.

The complexes show the characteristic shifts observed for diene complexes,^{10–12,18} viz., a very large upfield shift of the “terminal” carbon (C4) and a smaller but still large upfield shift of the “central” carbons (C2 and C3).

A comparison between benzylideneacetone and cinnamaldehyde, as free compounds and in the iron carbonyl complexes, showed the same substituent effects on the chemical shift of C3 upon substitution of the methyl group at C2 (β -effect) observed for dienes,¹⁰ indicating a greater π -bond order at the central C–C bond in the complexes.

Discussion

Carbonyl Resonances and Structure in Solution. The resonances of the carbonyls in the (BDA)Fe(CO)₂L complexes are shown in Table I and are assigned on the basis of the following arguments.

(a) For the (butadiene)Fe(CO)₃ complex only one resonance at 213.2 ppm is observed at 0 °C. At -80 °C this single peak is split into two resonances of relative intensities 1:2, at 217.4 and 211.3 ppm, unequivocally assigned to the apical and basal carbonyls, respectively.¹¹

(b) The average chemical shift of the carbonyls in (BDA)Fe(CO)₃ at 32 °C is 207.0 ppm, ca. 6 ppm to high field compared to that of (butadiene)Fe(CO)₃, and at -39 °C three resonances at 209.6, 208.7, and 202.9 ppm are observed.

(c) Substitution of one carbonyl by a phosphorus ligand in the (BDA)Fe(CO)₂L complexes increases the chemical shift of the remaining carbonyls by ca. 5–7 ppm. A similar effect was observed for (cyclohexadiene)Fe(CO)₂L complexes.¹⁰

It is not reasonable to assign the two carbonyl resonances of (BDA)Fe(CO)₃ at ca. 209 ppm to the basal positions since in (butadiene)Fe(CO)₃ the apical carbonyl resonance is ca. 6 ppm to low field compared to those of the basal carbonyls. A reasonable assignment would be as follows: $\delta(\text{CO})$ 209.6 or 208.7, apical position; $\delta(\text{CO})$ 202.9, basal position cis to the O atom of BDA; $\delta(\text{CO})$ 208.7 or 209.6 basal position trans to the O atom of BDA. In this case, the resonance of one of the carbonyls in the basal position is ca. 6 ppm less than that of the one in the apical position, as is the general case with diene complexes, and the other basal carbonyl is deshielded by ca. 6 ppm by the effect of the heteroatom in the trans position.

Assuming that the two basal carbonyls have a ¹³C chemical shift difference of ca. 6 ppm because of the effect of the heteroatom, one can explain the results observed for the complexes of BDA with phosphorus ligands. The ¹³C NMR spectra do not show any evidence for geometric isomers, and one can assume that the structure in solution is the same as in the solid state,¹³ with the phosphorus atom in the apical position. As a typical example, (BDA)Fe(CO)₂PEt₃ has resonances at $\delta(\text{CO})$ 215.6 ($J_{\text{PC}} = 14$ Hz) and $\delta(\text{CO})$ 210.1 ($J_{\text{PC}} = 0$ Hz). The entrance of the phosphine in the apical position would equally deshield the other two carbonyls in positions cis to the phosphorus by 6 ppm without altering the additional deshielding effect by the oxygen atom on the carbonyl in the trans position. Deshielding of the carbonyl resonance has generally been attributed to an increase in π back-donation from the metal atom to the carbonyl group.¹⁹ In

(18) Preston, H. G.; Davies, J. C. *J. Am. Chem. Soc.* **1966**, *88*, 1585–1586. Reicofsky, H. L.; Frankel, E. N.; Gutowsky, H. S. *Ibid.* **1966**, *88*, 2710–2712.

(17) Salvage, T.; Dixon, J. P. *Analyst (London)* **1965**, *90*, 24–28.

Table I. ^{13}C Chemical Shifts of the Benzylideneacetone and Carbonyl Resonances in $(\text{BDA})\text{Fe}(\text{CO})_2\text{L}^a$

L	C1	C2	C3	C4	C1'	C2'	C3'	C4'	CO ^b
CO ^c	20.9	142.3	77.8	60.7	138.8	126.5	128.6	126.7	207, broad
CO (-39 °C) ^c	21.1	141.1	78.2	60.5	138.2	126.5	128.6	126.5	202.9, 208.7, 209.6
P(OPh) ₃	21.1	141.4	78.3	59.9	140.6	127.6	128.6	126.1	207.0, 212.0 (15)
P(OMe) ₃	21.2	141.8	78.2	57.5	138.4	127.2	128.3	125.6	209.1 (12), 214.1 (18)
P(OEt) ₃	21.3	142.1	78.2	57.9	138.2	127.2	128.4	125.5	<i>d</i>
PPh ₃	21.5	142.3	79.7	63.0	139.5	126.7	128.3	125.4	209.8, 214.5 (10)
PMePh ₂	21.7	142.1	79.3	60.8	139.2	126.5	128.4	125.3	209.2, 214.7 (12)
P(<i>o</i> -tol) ₃	21.7	142.3	78.6	60.2	138.7	126.5	128.6	125.6	209.0 ^c
PMe ₂ Ph	21.6	142.5	78.7	59.4	139.7	126.5	128.5	125.2	209.0, 214.7 (14.5)
PEt ₃	21.5	143.3	78.6	57.4	138.9	126.9	128.5	125.0	210.0, 215.6 (14)
PCy ₃ ^c	21.5	142.6	80.0	56.8	133.6	126.4	128.0	124.4	<i>d</i>

^a Chemical shifts are in ppm relative to Me₄Si. Benzene-*d* solutions were used unless otherwise indicated; see structure 1 for atom numbering. ^b Spin-spin couplings (*J_p*). ^c In CDCl₃. ^d Not observed.

Table II. ^{13}C Complex Shifts Δ of Benzylideneacetone in $(\text{BDA})\text{Fe}(\text{CO})_2\text{L}^a$

L	C1	C2	C3	C4	C1'	C2'	C3'	C4'	$\Delta\text{C4}/\Delta\text{C3}$
CO	-6.5	-54.3	-49.7	-81.8	3.9	-1.9	-0.4	-3.6	1.65
P(OPh) ₃	-6.3	-55.2	-49.2	-82.6	5.7	-0.8	-0.4	-4.2	1.68
P(OMe) ₃	-6.2	-54.8	-49.3	-85.0	3.5	-1.3	-0.7	-4.7	1.72
P(OEt) ₃	-6.1	-54.5	-49.1	-84.6	3.3	-1.2	-0.6	-4.8	1.72
PPh ₃	-5.9	-54.3	-47.8	-79.5	4.6	-1.7	-0.7	-4.9	1.66
PMePh ₂	-5.7	-54.5	-48.2	-81.7	4.3	-1.9	-0.6	-5.0	1.68
P(<i>o</i> -tol) ₃	-5.7	-54.3	-48.9	-82.3	3.8	-1.9	-0.4	-4.7	1.68
PMe ₂ Ph	-5.8	-54.1	-48.8	-83.1	4.8	-1.9	-0.5	-5.0	1.70
PEt ₃	-5.9	-53.3	-48.9	-85.1	4.0	-1.5	-0.5	-5.3	1.74
PCy ₃	-5.9	-54.0	-47.5	-85.7	-1.3	-2.0	-1.0	-5.9	1.80

^a $\Delta = \delta(\text{complex}) - \delta(\text{free ligand})$.

the X-ray study of $(\text{BDA})\text{Fe}(\text{CO})_2\text{PEt}_3$,¹³ it was observed that the Fe-C(carbonyl) bond distance trans to the oxygen atom of BDA is shorter than the Fe-C(carbonyl) bond trans to the "outer" diene carbon of BDA, suggesting a greater Fe-CO back-bonding from the iron atom to the carbonyl group trans to oxygen.

The results show a dramatic increase in the barrier to carbonyl rearrangement in $(\text{BDA})\text{Fe}(\text{CO})_2\text{L}$ (L = CO, phosphine, phosphite) in comparison with that in $(\text{diene})\text{Fe}(\text{CO})_3$ complexes. For example, $(\text{butadiene})\text{Fe}(\text{CO})_3$ has a coalescence temperature for the carbonyl resonances in the ^{13}C spectrum of -65 °C²⁰ while the BDA complexes with a phosphorus ligand do not show any fluxional behavior at 32 °C. The $(\text{BDA})\text{Fe}(\text{CO})_3$ complex is fluxional at 32 °C but the line width of ca. 100 Hz indicates that the coalescence temperature is only slightly lower, probably very similar to that of $(\text{cinnamaldehyde})\text{Fe}(\text{CO})_3$, which is 25 °C.¹² Since the separations between the carbonyl resonances in these complexes are comparable, the coalescence temperatures are a reliable measure of the relative magnitudes of the barrier.

The large barrier in $(\text{BDA})\text{Fe}(\text{CO})_2\text{L}$ compared with that in $(\text{butadiene})\text{Fe}(\text{CO})_3$ appears to be due to the combined effects of the heterodiene and phosphorus ligands. The barrier to rearrangement is determined by both the ground state and the transition state. In the ground state, the presence of the electron-withdrawing oxygen atom in the conjugated system of the BDA ligand would lower the energies of both HOMO and LUMO MO's with respect to the corresponding orbitals of butadiene.²¹ This brings the energy of the LUMO closer to the energies of the filled metal d orbitals, making BDA a better acceptor than butadiene relative to the $\text{Fe}(\text{CO})_3$ moiety.²² It has been previously suggested that an increase in the acceptor ability of dienes increases the barrier as a consequence of increasing the six-coordinate character.¹¹ The substitution of the CO in the apical position by the better σ -donor and poorer π -acceptor phosphorus ligands would

increase the flow of metal electron density into the LUMO of BDA, further increasing the six-coordinate character and the barrier.

Coordinated BDA Resonances and Electronic Effects. The very large upfield shifts of the carbon atoms of BDA involved in bonding with $\text{Fe}(\text{CO})_3$ are expected since this moiety acts as a net electron donor to diene ligands.^{3,4} The origin of the large upfield shifts of olefins upon complexation to transition metals has still not been clearly established.²³ Apparently, various factors contribute to the complex shift; however, the interpretation based on the Dewar-Chatto-Duncanson model of bonding in metal-olefin complexes has proved useful.²⁴ In this interpretation the metal to ligand π^* interaction would (i) increase the total electron density at the olefinic carbon and (ii) reduce the carbon-carbon π -bond order and hence the π character of these carbons. The ligand to metal dsp bonding would (iii) decrease the π character and (iv) decrease the electron density at the olefinic carbon. Since only case iv will have a deshielding effect, it was suggested that there will be a net shielding effect that correlates closely with the electron density on the metal and metal to olefin π^* interaction.

The bonding capability of the $\text{Fe}(\text{CO})_3$ fragment is discussed in detail by Elian and Hoffmann.⁴ The valence shell of the $\text{Fe}(\text{CO})_3$ fragment, which has a symmetry of C_{3v} , presents to a potential ligand a set of three hybridized orbitals, two of which are degenerate and accommodate a high-energy electron pair.^{25,26} Diene ligands can provide a good donor orbital (HOMO) with the symmetry of one of the components of the e level of $\text{Fe}(\text{CO})_3$ and a good acceptor orbital (LUMO) with the symmetry of the other e orbital; interaction between these orbitals would split the e level and provide the stabilization that a distortion of this fragment would produce. As it was previously pointed out, the energies of both the HOMO and LUMO of BDA are lower than those of the corresponding orbitals of butadiene, making the BDA a better acceptor for the electrons of $\text{Fe}(\text{CO})_3$. On the other hand,

- (19) Gansow, O. A.; Schexnayder, D. A.; Kimura, B. Y. *J. Am. Chem. Soc.* **1972**, *94*, 3406-3408. Bodner, G. M.; Todd, L. J. *Inorg. Chem.* **1974**, *13*, 1335-1338. Bodner, G. M. *Ibid.* **1974**, *13*, 2563-2566.
 (20) Kreiter, C. G.; Stüber, S.; Wackerle, L. J. *Organomet. Chem.* **1974**, *66*, C49-C52.
 (21) Fleming, I. "Frontier Orbitals and Organic Chemical Reactions"; Wiley: London, 1976; p 115.
 (22) For a detailed discussion of the bonding capability of the $\text{Fe}(\text{CO})_3$ fragment, see ref 4.

- (23) Jolly, P. W.; Mynott, R. *Adv. Organomet. Chem.* **1981**, *19*, 257-304 and references therein.
 (24) Chisholm, M. H.; Clark, H. C.; Manzer, L. E.; Stothers, J. B. *J. Am. Chem. Soc.* **1972**, *94*, 5087-5089.
 (25) Wade, K. J. *Chem. Soc. D* **1971**, 792-793; *Inorg. Nucl. Chem. Lett.* **1972**, *8*, 559-562; "Electron Deficient Compounds"; Nelson: London, 1971.
 (26) Mingos, D. M. P. *Nature (London) Phys. Sci.* **1972**, *236*, 99-100.

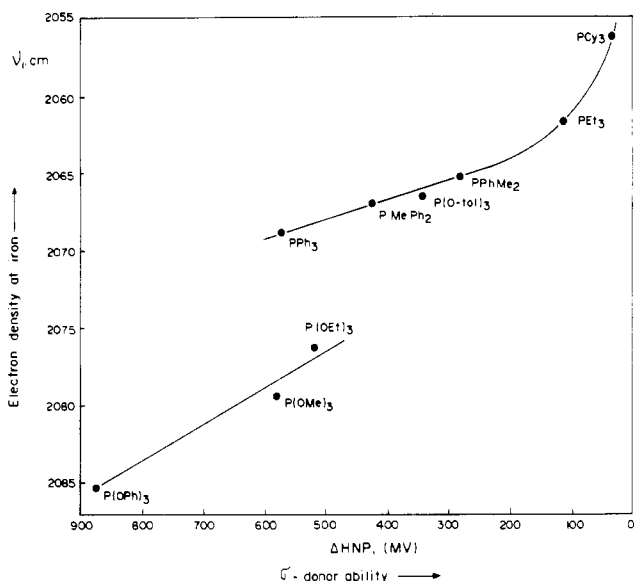


Figure 1. Correlation between the Tolman electronic parameter ν and the half-neutralization potentials ΔHNP of the phosphine and phosphite ligands.

the coefficients of the atomic orbitals in the LUMO of BDA increase at the "terminal" carbon (C4) and decrease at the "central" carbon (C3) with respect to butadiene.²⁷ The contrary is observed for the HOMO of BDA compared to that of butadiene. In other words, the BDA molecule has its bonding participating MO's polarized in such a way that the oxygen atom may be considered as the major electron-donor center and the carbon atom C4 as the major electron-acceptor center in binding with $\text{Fe}(\text{CO})_3$. In valence bond terms of the structural extremes **2a** and **2b**, the valence state of BDA in the complex will have a substantial contribution from structure **2b**.

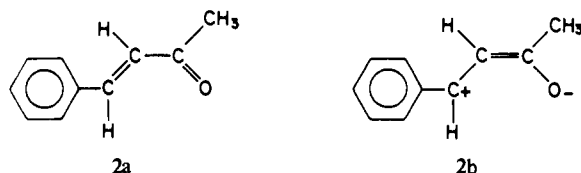


Table II shows the difference, Δ , between the chemical shifts of complexed and free BDA (complex shift). It is interesting to compare these values with the ones observed for (butadiene) $\text{Fe}(\text{CO})_3$. For instance, ΔC4 increases from -75.5 ppm for (butadiene) $\text{Fe}(\text{CO})_3$ ²⁸ to -81.1 ppm for (BDA) $\text{Fe}(\text{CO})_3$, following the increase in the π -acceptor ability of the ligand. The relative complex shift $\Delta\text{C4}/\Delta\text{C3}$ increase from 1.47 for (butadiene) $\text{Fe}(\text{CO})_3$ ²⁸ to 1.62 for (BDA) $\text{Fe}(\text{CO})_3$, following the increase in the polarization of C4–C3 double bond.

The mechanism discussed above is certainly not the only factor and possibly not even the predominant one responsible for the complex shift. However, the small trends in the complex shifts of the closely related series of complexes (BDA) $\text{Fe}(\text{CO})_2\text{L}$ are consistent with this interpretation.

Complex Shifts Induced by the Phosphorus Ligands. The ability of the $\text{Fe}(\text{CO})_2\text{L}$ fragments to donate electron density to the BDA ligand will depend on the σ -donor– π -acceptor properties of the phosphorus ligands, which can be measured by the Tolman electronic parameter.²⁹ The σ -donor ability of the phosphorus ligands can be estimated in terms of its basicity. Figure 1 shows plots of the Tolman electronic parameter, ν , vs. the Streuli relative proton basicities, ΔHNP ,³⁰ of the phosphorus ligands studied in

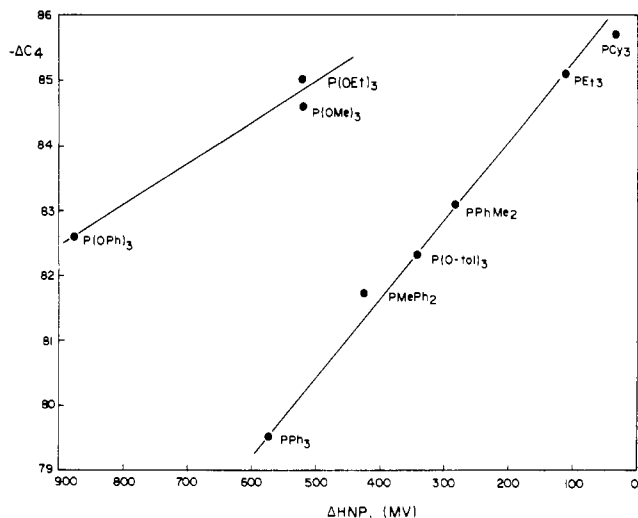


Figure 2. Correlation between the ^{13}C complex shift of C4 in benzylideneacetone in the complex (BDA) $\text{Fe}(\text{CO})_2\text{L}$ and the half-neutralization potential ΔHNP of the phosphorus ligands, which is a measure of their basicities.

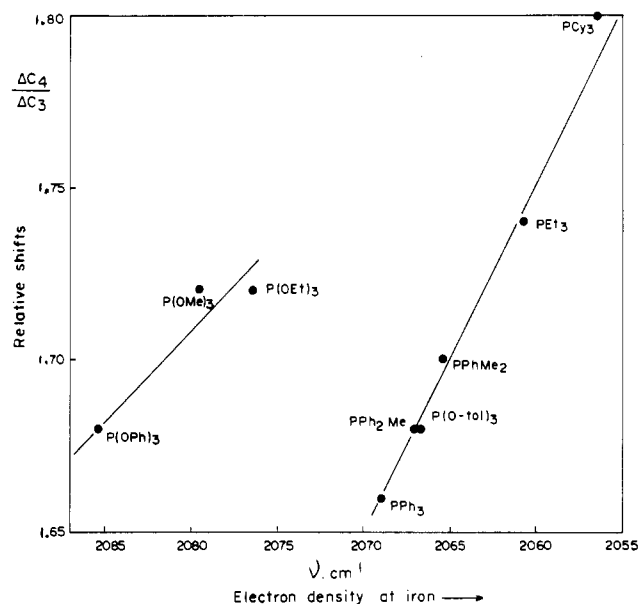


Figure 3. Correlation between the ratio of the ^{13}C complex shifts $\Delta\text{C4}/\Delta\text{C3}$ of the benzylideneacetone ligand in the complex (BDA) $\text{Fe}(\text{CO})_2\text{L}$ and the Tolman electronic parameter ν of the phosphorus ligands, which reflects the electron density on the iron atom.

this work. The correlation is almost linear for the aromatic phosphines, but ν increases more sharply with ΔHNP for the aliphatic phosphines. If ν is taken as a measure of the relative electron density at the metal atom, the mesomeric effect of the phenyl groups will expand the phosphorus d_π orbitals and thus increase the metal–phosphorus π back-donation, reducing the electron density at the metal atom.

The shielding at carbon C4 will depend on the overlap between the LUMO of BDA and the filled metal orbitals. An increase in the σ -donor ability of the phosphorus ligand is expected to expand these filled orbitals, improving the overlap. Figure 2 shows that $-\Delta\text{C4}$ correlates linearly with ΔHNP , suggesting that iron–phosphorus π back-bonding does not interfere with the metal–BDA π^* interaction. The complex shifts of the phosphites are greater than those expected on the basis of their ΔHNP values. This can be interpreted by keeping in mind that ΔHNP measures the proton–phosphite σ interaction. In bonding with iron, the $d-d_\pi$

(27) Fleming, I. "Frontier Orbitals and Organic Chemical Reactions"; Wiley: London, 1976; p 124.

(28) Calculated from data in Table II of ref 11.

(29) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2953–2956; *Chem. Rev.* **1977**, *77*, 313–348.

(30) Streuli, C. A. *Anal. Chem.* **1960**, *32*, 985–987. Chang, C. Y.; Johnson, C. E.; Richmond, T. G.; Chen, Y. T.; Troglor, W. C.; Basolo, F. *Inorg. Chem.* **1981**, *20*, 3167–3171 and references therein.

back-bonding to the phosphites, which is greater than the d-d_π back-bonding to the phosphines, would produce a bigger synergic increase in the σ donation, increasing the shielding at carbon C4.

According to the bonding scheme proposed, the overall electron density at the metal atom is controlled by the interactions of the metal orbitals with the HOMO and LUMO of BDA and with the σ and π orbitals of carbon monoxide and phosphorus ligands. It can be seen in Table I that there are no significant trends in the chemical shifts of the carbonyls within the series. This suggests that the changes in the electron density at the metal atom are controlled mainly by the interactions of the iron orbitals with the orbitals of BDA and phosphorus ligands. Plots of ΔC4/ΔC3 vs. ν presented in Figure 3 show that the relative complex shifts increase linearly with the overall electron density at the metal atom. The effect is larger for the phosphites than for the phosphines. This is again contrary to that expected on the basis of the greater iron-phosphorus π back-bonding in the phosphite complexes. An explanation could be given on the basis of a stronger interaction between the HOMO of BDA and the empty metal orbitals in the phosphite complexes. Since the oxygen atom is the major donor center and the C4 carbon atom the major acceptor center of BDA, the effect on ΔC4/ΔC3 would reflect a net transfer of electron density from the oxygen atom to the C4 carbon atom through the iron atom.

The results discussed above seem to indicate that the BDA ligand acts as a "sink" for the negative charge placed on the iron atom by the phosphorus ligand via a P←Fe←BDA mechanism. This is in contrast with that observed in (π-cyclopentadienyl)iron carbonyl complexes.¹⁹ In these complexes, the iron-cyclopentadienyl π back-bonding is not important and the electronic effects of the substituents on the cyclopentadienyl group are transmitted to the carbonyls.

On the basis of the results discussed in this paper we agree with Pearson and Raithby¹⁰ that ¹³C NMR spectroscopy provides an exceedingly sensitive means of detecting relatively small electronic perturbations in organometallic systems that are not always possible to detect by X-ray methods.

Acknowledgment. We thank the Conselho Nacional de Desenvolvimento Científico (CNPq), Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP), and Financiadora de Estudos e Projetos (FINEP) for financial support.

Registry No. (BDA)Fe(CO)₃, 38720-22-8; (BDA)Fe(CO)₂P(OPh)₃, 93984-14-6; (BDA)Fe(CO)₂P(OMe)₃, 93984-15-7; (BDA)Fe(CO)₂P(OEt)₃, 93923-25-2; (BDA)Fe(CO)₂PPh₃, 93984-16-8; (BDA)Fe(CO)₂PMePh₂, 88760-06-9; (BDA)Fe(CO)₂P(o-tol)₃, 93923-26-3; (BDA)Fe(CO)₂PMe₂Ph, 89230-56-8; (BDA)Fe(CO)₂PEt₃, 89230-55-7; (BDA)Fe(CO)₂PCy₃, 93923-27-4; Fe(CO)₄PCy₃, 18474-81-2; Fe(CO)₄P(o-tol)₃, 40697-06-1; dodecacarbonyltriiron, 17685-52-8.

Contribution from the Department of Chemistry,
University of California, Davis, California 95616

Mono- and Polynuclear Transition-Metal Complexes of the Linear, Small-Bite Tris(phosphine) Bis((diphenylphosphino)methyl)phenylphosphine

ALAN L. BALCH,* ROSALVINA R. GUIMERANS, and JOHN LINEHAN

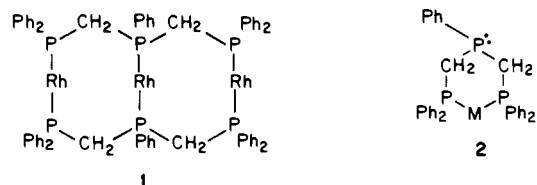
Received May 21, 1984

Bis((diphenylphosphino)methyl)phenylphosphine (dpmp) forms chelated complexes Pt(dpmp)(CH₃)₂, Pt(dpmp)(CN)₂, Pd(dpmp)X₂ (X = Cl, Br, I) and M(dpmp)(CO)₄ (M = Cr, Mo, W) in which the internal phosphorus atom is uncoordinated. Spectroscopic characterization by ³¹P and ¹H NMR and infrared is reported. In solution, Pd(dpmp)X₂ (X = Cl, Br) reacts with itself to form PdX₂(μ-dpmp)Pd(dpmp)X₂, which has been identified by ³¹P NMR spectroscopy. These chelated monomers react with other d⁸ metal ions to form trinuclear complexes: *trans*-Rh(CO)Cl[(μ-dpmp)ML_n]₂, ML_n = Pt(CH₃)₂, PtCl₂, PdCl₂, Mo(CO)₄; *cis*-PtCl₂[(μ-dpmp)ML_n]₂, ML_n = Pt(CH₃)₂, PdCl₂, Mo(CO)₄; *trans*-PdCl₂[(μ-dpmp)ML_n]₂, ML_n = Pt(CH₃)₂, PdCl₂, Mo(CO)₄. NMR spectroscopic properties indicative of the formation of these trinuclear complexes include a downfield shift of the ³¹P resonance of the internal phosphorus atom of dpmp, a reduction of J(P,P) from 60–80 Hz in the bidentate chelates to less than 5 Hz in the dpmp-bridged complexes, and increased complexity in the upfield methylene resonance in the ¹H NMR spectrum. The metal centers appear to be remote from one another and noninteracting in these trinuclear complexes.

Introduction

While the behavior of polydentate ligands toward a single metal center has been an area of careful, detailed study for a long time,¹ the binding of polydentate ligands to several metal centers has only recently begun to be studied. Polydentate ligands, particularly poly(phosphine) ligands, can be used to prepare^{2,3} and stabilize⁴ metal clusters, to promote metal-metal interactions,⁵ and to facilitate the formation of novel ligand bridges between metal centers.⁶

In this article we are concerned with the behavior of the linear, small-bite tris(phosphine) bis((diphenylphosphino)methyl)phenylphosphine (dpmp), in the context of building complex structures from monomeric fragments. Two questions emerge in this context. How does this ligand prefer to bind a single metal ion? How can these monomeric poly(phosphine) complexes be used to create new multicentered assemblages? We have demonstrated that this ligand is capable of forming a group of reactive trirhodium complexes in which the framework, **1**, remains intact



- (1) Hawkins, C. J. "Absolute Configuration of Metal Complexes"; Wiley-Interscience: New York, 1982. Meek, D. W. In "Homogeneous Catalysis with Metal Phosphine Complexes"; Pignolet, L. H., Ed.; Plenum Press: New York, 1983; p 257.
- (2) Guimerans, R. R.; Olmstead, M. M.; Balch, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 1677.
- (3) Wood, F. E.; Olmstead, M. M.; Balch, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 6332.
- (4) Mague, J. T.; Dessens, S. E. *J. Organomet. Chem.* **1984**, *262*, 347 and references therein.
- (5) Balch, A. L. In "Reactivity of Metal-Metal Bonds"; Chisholm, M., Ed.; American Chemical Society: Washington, DC, 1981; ACS Symp. Ser. No. 155, pp 167-185.
- (6) Balch, A. L. In "Homogeneous Catalysis with Metal Phosphine Complexes"; Pignolet, L. H., Ed.; Plenum Press: New York, 1983; p 167.

while other ligands, which coordinate perpendicularly to this unit, readily undergo substitution and exchange.^{2,7-9} Additionally dpmp

- (7) Olmstead, M. M.; Guimerans, R. R.; Balch, A. L. *Inorg. Chem.* **1983**, *22*, 2473.
- (8) Balch, A. L.; Olmstead, M. M.; Guimerans, R. R. *Inorg. Chim. Acta* **1984**, *84*, L21.