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New Complexes of Methyldiphenylphosphonium Cyclopentadienylide, Representative of a Class of Ligands Heretofore Much Neglected

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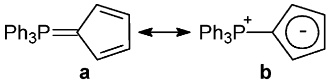
Methyldiphenylphosphonium cyclopentadienylide, $C_5H_4PMePh_2$ (**II**), has been synthesized and characterized spectroscopically and crystallographically and has been found to exhibit properties consistent with the zwitterionic structure **IIb**. The new group 6 coordination complexes $(\eta^5\text{-}C_5H_4PMePh_2)M(CO)_3$ have been synthesized via substitution reactions of **II** with $M(CO)_6$ (M = Cr, Mo) or $W(CO)_3(MeCN)_3$. Comparisons of $\nu(CO)$ values of these complexes with those of the isoelectronic $(\eta^6\text{-}C_6H_6)M(CO)_3$ and $[(\eta^5\text{-}C_5H_5)M(CO)_3]^-$ suggest that the electron-donating ability of the ylide is less than that of the cyclopentadienyl anion but much greater than that of benzene. Thermal and photochemical substitutions of the CO ligands of $(\eta^5\text{-}C_5H_4PMePh_2)M(CO)_3$ (M = Cr, Mo) by equimolar amounts of PMe_3 and PPh_3 were not observed, but the ylide is displaced photochemically from $(\eta^5\text{-}C_5H_4PMePh_2)Mo(CO)_3$ by excess PMe_3 to form *fac*-$Mo(CO)_3(PMe_3)_3$, while $(\eta^5\text{-}C_5H_4PMePh_2)Mo(CO)_3$ reacts with I_2 to form $[(\eta^5\text{-}C_5H_4PMePh_2)Mo(CO)_3I]I$. The crystal structures of the free ylide and all four of its coordination complexes show that in each case one of the ylide phenyl rings not only eclipses the C_5H_4 ring but also is oriented toward it in an edge-on fashion. The intramolecular edge−face orientations involve interactions of an aromatic hydrogen atom with the C_5H_4 aromatic π systems and are rationalized in terms of electrostatic attractive forces between the slightly positive phenyl hydrogen atom and the negatively charged C_5H_4 ring. The electronic structures of **II** and of $(\eta^5\text{-}C_5H_4PMePh_2)Cr(CO)_3$ have been investigated using ab initio methodologies; it is found that the near-degenerate HOMO and HOMO-1 orbitals of the free ylide exhibit symmetries very similar to those of the corresponding, doubly degenerate HOMO of the cyclopentadienyl anion (E_1 symmetry) and that a lower energy, almost fully symmetric orbital corresponds to the fully symmetric bonding A_1 MO of the cyclopentadienyl anion. In none of these three orbitals does there appear to be significant π involvement of an orbital on the phosphorus atom, consistent with the low P−C bond order implicit in the zwitterionic structure **IIb**. The primary ylide−metal interactions in $(\eta^5\text{-}C_5H_4PMePh_2)Cr(CO)_3$ involve donation of the HOMO and HOMO-1 orbitals into the d_{xz} and d_{yz} orbitals of the chromium, while the calculated ylide−$Cr(CO)_3$ bond dissociation energy is about 30% higher than the analogous ring−metal bond dissociation energy of $(\eta^6\text{-}C_6H_6)Cr(CO)_3$.

Triphenylphosphonium cyclopentadienylide (cyclopentadienylidene triphenylphosphorane) (**I**) was first reported in 1956 by Ramirez and Levy,[1a] who also explored its chemistry.[1b−f]



I

They found, inter alia, that **I** is unusually inert, for instance being unreactive with ketones, unlike ylides normally. They attributed this unusual stability to the charge delocalization implied by resonance structure **Ib**, consistent with the relatively high dipole moment of 7.0 D.[1c]

Further evidence for extensive delocalization of the π-electron density was found in the crystal structure, which showed significant shortening of the P−C_5H_4 bond,[1g] and in the ^{13}C NMR spectrum, which showed an unusually high field chemical shift for the ylide carbon and a P−C(ylide) coupling constant typical of an aliphatic carbon−P bond.[1h]

Wilkinson noted soon after the initial Ramirez report that, since **Ib** would be isoelectronic with benzene, the ylide might be expected to form compounds of the type $(\eta^5\text{-}C_5H_4PPh_3)M(CO)_3$ (M = Cr, Mo, W), analogous to the known arene compounds $(\eta^6\text{-}C_6H_6)M(CO)_3$. Successful attempts to prepare the group 6 compounds were carried out, and the molybdenum compound was obtained analytically pure,[2a] although the structures and chemistry of these compounds were only explored many years later.[2b−g] Analogous carbonyl complexes of manganese and rhenium, of the type $[(\eta^5\text{-}C_5H_4PPh_3)M(CO)_3]^+$ (M

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10.1021/om070018j CCC: $37.00

= Mn, Re),[3] and a cobalt complex, $[(\eta^5\text{-}C_5H_4PPh_3)Co(CO)_2]^+$,[4] have subsequently been reported, as have a few satisfactorily characterized complexes of **I** with ruthenium,[5a] rhodium,[5b,c] nickel,[5d] palladium,[5e−h] platinum,[5h] and mercury.[5i,j] However, a number of attempts to prepare complexes of metal halides generally resulted in poorly soluble species of indefinite constitution.[6]

In part, perhaps, because of difficulties in characterizing many of the compounds obtained, research in this area stagnated and virtually no publications dealing with the coordination chemistry of **I** have appeared in over two decades.[2−6] However, the donor properties of **I** and similar ligands are expected to fall between those of benzene and the cyclopentadienyl (Cp) ligand and, given the enormous importance of Cp and related complexes,[7] this lack of interest seems quite surprising. Furthermore, while complexes of **I** have been found to contain the ligand bound to the metal in an η^5 fashion, coordination in an η^1 fashion has been demonstrated[5i] and coordination could in principle also occur in the η^2, η^3, and η^4 modes. Thus, tertiary phosphine based cyclopentadienylidene ligands offer the possibility of exhibiting a range of interesting structures and catalytic reactivities, and we have embarked on a program to reopen the chemistry of this class of ligand.

Hoping to avoid the solubility problems apparently limiting development of the chemistry of **I**, we have chosen to investigate mixed alkyl−aryl cyclopentadienylidene derivatives which would also be more amenable to characterization by NMR spectroscopy. Since the original Ramirez synthetic procedure[1] turned out not to be generally applicable to other phosphines,[8] we are working initially with $C_5H_4PMePh_2$ (**II**), which we anticipated synthesizing from commercially available starting materials as in eqs 1−3.

$$PClPh_2 + NaCp \rightarrow PCpPh_2 \tag{1}$$

$$PCpPh_2 + MeI \rightarrow [PMeCpPh_2]I \tag{2}$$

$$[PMeCpPh_2]I + BuLi \rightarrow \underset{\textbf{II}}{C_5H_4PMePh_2} \tag{3}$$

We quickly found that **II** had been prepared previously via a similar route in which TlCp was used instead of NaCp[9] but that the free ylide had been neither thoroughly characterized nor investigated with respect to its coordination chemistry. We have therefore developed a reliable synthetic procedure for **II** and report here the complete spectroscopic and crystallographic characterization of this compound. We also describe the syntheses and characterization and some chemistry of the group 6 compounds $(\eta^5\text{-}C_5H_4PMePh_2)M(CO)_3$ (M = Cr, Mo, W), a series chosen for our initial study because the group 6 tricarbonyl complexes of **I** are known[2] and we wished to be able to make direct comparisons of the coordination chemistry of **I** and **II**. We have also investigated, via ab initio calculations, the nature of the bonding in **II** and of its complex $(\eta^5\text{-}C_5H_4PMePh_2)Cr(CO)_3$.

Experimental Section

All syntheses were carried out under a dry, deoxygenated argon atmosphere using standard Schlenk line techniques. Argon was deoxygenated by passage through a heated column of BASF copper catalyst and then dried by passing through a column of 4A molecular sieves. Handling and storage of air-sensitive organometallic compounds was done using an MBraun Labmaster glovebox. NMR spectra were recorded using Bruker AV 300, AV 500, and AV 600 spectrometers. All ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to carbons or residual protons present in the deuterated solvents with respect to TMS at δ 0. ^{31}P NMR was referenced to external 85% H_3PO_4. Elemental analyses were conducted by Canadian Microanalytical Service Ltd., Delta, BC, Canada.

Anhydrous methylene chloride, THF, diethyl ether, hexanes, and toluene were purchased from Aldrich in 18 L reservoirs packaged under nitrogen and were dried by passage through columns of activated alumina (Innovative Technology Solvent Purification System). THF, Et_2O, and CH_2Cl_2 were then stored over 4A molecular sieves to result in residual water concentrations that were lower than 20 ppm. NMR solvents used for organometallic compounds were degassed under vacuum and dried by passage through a small column of activated alumina before being stored over 4A molecular sieves. All deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc., or CDN Isotopes. Most chemicals were obtained from Aldrich or Strem and were used as received or purified by established procedures.

X-ray crystal structure determinations were performed by Dr. Ruiyao Wang in the X-ray Crystallography Laboratory at Queen's University. Crystals were mounted on glass fibers with epoxy glue, and data collection was performed on a Bruker Smart CCD 1000 X-ray diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) controlled with a Cryostream Controller 700. No significant decay was observed during data collections. Data were processed on a Pentium PC using the Bruker AXS Crystal Structure Analysis Package, Version 5.10.[10a] Neutral atom scattering factors were taken from Cromer and Waber.[10b] The raw intensity data were converted (including corrections for scan speed, back-

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ground, and Lorentz and polarization effects) to structure amplitudes and their esds using the program SAINT, which corrects for *Lp* and decay. Absorption corrections were applied using the program SADABS. All non-hydrogen atoms were refined anistropically. The positions for all hydrogen atoms were calculated (unless otherwise stated), and their contributions were included in the structure factors and calculations.

Synthesis of $C_5H_4PMePh_2$ (II). A suspension of 20.0 g of TlCp (0.074 mol) in 200 mL of ether was treated dropwise with 13.3 mL of Ph_2PCl (0.073 mol). As the reaction proceeded, the flask warmed and the solution turned slightly yellow. After it was stirred for 1 h, the reaction mixture was filtered to remove TlCl, and the phosphine, $P(C_5H_5)Ph_2$, was immediately treated in situ with 4.5 mL of MeI (0.072 mol). As the alkylation reaction proceeded, a white product precipitated. The reaction mixture was stirred for 3 h, and 22.9 g of the white phosphonium salt ($[PMe(C_5H_5)Ph_2]I$) was collected by filtration in 81% yield. The product was impure (NMR), but attempts to purify it proved fruitless and the salt was therefore used as obtained in the next step.

To prepare **II**, a suspension of 10.1 g of $[PMe(C_5H_5)Ph_2]I$ (0.26 mol) in 150 mL of THF was cooled in an ice bath and treated dropwise with 17.7 mL of 1.6 M *n*-BuLi in hexanes (0.028 mol). As the *n*-BuLi was added, the solution warmed and the solid disappeared, generating a deep orange-red solution. The reaction was stirred until no solid remained, at which point the reaction was hydrolyzed by the addition of 20 mL of H_2O. This caused the formation of a white solid, while the solution turned yellow. The organic layer was decanted, and the aqueous layer was washed with 3 × 75 mL of toluene. The organic layers were combined, and the solvent was removed in vacuo to yield an orange solid which was extracted with 200 mL of ethyl acetate and passed through a silica column using ethyl acetate as the eluent. The yellow band was collected, and the solvent was removed under reduced pressure to yield 2.1 g (30% based upon phosphonium salt) of $C_5H_4PMePh_2$ (**II**) as a yellow powder. X-ray-quality crystals and analytically pure material were obtained by crystallization from CH_2Cl_2 solution at -30 °C by layering with hexanes. This procedure has been repeated many times with yields ranging from 20 to 35%. ^1H NMR of **II** ($CDCl_3$, 500 MHz): δ 7.64−7.59 (6H, m, Ph), 7.52−7.49 (4H, m, Ph), 6.44 (2H, m, PCCHC*H*), 6.29 (2H, m, PCC*H*CH), 2.37 (3H, d, $^2J_{H-P} = 13.2$ Hz, Me). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 132.6 (d, $^4J_{P-C} = 2.1$ Hz, *p*-Ph), 132.3 (d, $J_{P-C} = 10.6$ Hz, Ph), 129.0 (d, $J_{P-C} = 11.5$ Hz, Ph), 127.5 (d, $^1J_{P-C} = 88.3$ Hz, *ipso*-Ph), 114.9 (d, $^2J_{P-C} = 16.3$ Hz, PC*C*HCH), 114.3 (d, $^3J_{P-C} = 17.3$ Hz, PCCHC*H*), 79.2 (d, $^1J_{P-C} = 114.2$ Hz, P*C*), 12.6 (d, $^1J_{P-C} = 63.3$ Hz, Me). ^{31}P NMR ($CDCl_3$, 121 MHz): δ 7.95. Anal. Found: C, 80.76; H, 6.56. Calcd: C, 81.80; H, 6.48.

Synthesis of (η^5-$C_5H_4PMePh_2$)$Cr(CO)_3$ (III). A solution of 0.39 g of **II** (1.5×10^{-3} mol) and 0.96 g of $Cr(CO)_6$ (4.4×10^{-3} mol) in 30 mL of diglyme was refluxed under argon for 3 h, during which time the solution developed a black-green color. The reaction mixture was cooled and filtered, and the solid residue was washed with 3 × 10 mL of diglyme. The resulting filtrate was then treated with 200 mL of hexanes to precipitate a yellow solid that was collected and washed with hexanes (3 × 10 mL). The solid was dried in vacuo to yield 0.35 g (61%) of yellow product. X-ray-quality crystals and analytically pure material were obtained by crystallization from CH_2Cl_2 solution at -30 °C by layering with hexanes. ^1H NMR (CD_2Cl_2, 500 MHz): δ 7.75−7.63 (10H, m, Ph), 4.90 (2H, br, PCCHC*H*), 4.71 (2H, br, PCC*H*CH), 2.55 (3H, d, $^2J_{H-P} = 13.2$ Hz, Me). ^{13}C NMR (CD_2Cl_2, 125 MHz): δ 241.8 (Cr−*C*O), 134.8 (d, $^4J_{P-C} = 2.2$ Hz, *p*-Ph), 133.3 (d, $J_{P-C} = 11.1$ Hz, Ph), 130.2 (d, $J_{P-C} = 12.3$ Hz, Ph), 123.1 (d, $^1J_{P-C} = 90.2$ Hz, *ipso*-Ph), 89.9 (d, $^2J_{P-C} = 13.4$ Hz, PC*C*HCH), 87.5 (d, $^3J_{P-C} = 13.4$ Hz, PCCHC*H*), 65.8 (d, $^1J_{P-C} = 111.4$ Hz, PC), 12.8 (d, $^1J_{P-C} = 65.7$ Hz, Me). ^{31}P NMR (CD_2Cl_2, 121 MHz): δ 19.54. Anal. Found: C, 62.51; H, 4.17. Calcd: C, 63.01; H, 4.28. IR (CH_2Cl_2): 1915, 1812 cm^{-1}.

The compound (η^5-$C_5H_4PMePh_2$)$Mo(CO)_3$ (**IV**) was prepared and purified similarly using 0.40 g of **II** (1.5×10^{-3} mol) and 1.21 g of $Mo(CO)_6$ (4.6×10^{-3} mol). The yellow product was obtained in 60% yield (0.41 g). ^1H NMR (CD_2Cl_2, 500 MHz): δ 7.77 (2H, t, $^3J_{H-H} = 7.1$ Hz, Ph), 7.71−7.62 (8H, m, Ph), 5.48 (2H, m, PCCHC*H*), 5.29 (2H, m, PCC*H*CH), 2.55 (3H, d, $^2J_{H-P} = 13.6$ Hz, Me). ^{13}C NMR (CD_2Cl_2, 125 MHz): δ 231.2 (Mo−*C*O), 135.0 (d, $^4J_{P-C} = 2.9$ Hz, *p*-Ph), 133.4 (d, $J_{P-C} = 10.6$ Hz, Ph), 130.2 (d, $J_{P-C} = 12.5$ Hz, Ph), 122.5 (d, $^1J_{P-C} = 90.2$ Hz, *ipso*-Ph), 94.5 (d, $^2J_{P-C} = 14.4$ Hz, PC*C*HCH), 92.1 (d, $^3J_{P-C} = 12.5$ Hz, PCCHC*H*), 71.8 (d, $^1J_{P-C} = 109.4$ Hz, P*C*), 14.4 (d, $^1J_{P-C} = 66.2$ Hz, Me). ^{31}P NMR (CD_2Cl_2, 121 MHz): δ 18.25. Anal. Found: C, 56.81; H, 3.76. Calcd: C, 56.77; H, 3.86. IR (CH_2Cl_2): 1918, 1812 cm^{-1}.

The tungsten analogue (η^5-$C_5H_4PMePh_2$)$W(CO)_3$ (**V**) was prepared by reacting 0.11 g of **II** (4.1×10^{-4} mol) and 0.40 g of $W(MeCN)_3(CO)_3$ (1.0×10^{-3} mol) in 20 mL of diglyme at 110 °C for 40 h. The solution turned a black-green color, and a black precipitate formed. The reaction mixture was cooled, the solvent was removed under reduced pressure, and the resulting gray-green solid was dissolved in degassed $CHCl_3$ and passed through an alumina column under an argon atmosphere. The yellow band was collected, and the solvent was removed in vacuo to yield 0.15 g (70%) of yellow product. X-ray-quality crystals were obtained by crystallization from CH_2Cl_2 at -30 °C by layering with hexanes, but several attempts to recrystallize the bulk product failed to remove a small amount of impurity, which exhibited a similar ^1H NMR spectrum and similar solubility properties. ^1H NMR (CD_2Cl_2, 500 MHz): δ 7.78 (2H, t, $^3J_{H-H} = 7.0$ Hz, Ph), 7.71−7.62 (8H, m, Ph), 5.46 (2H, m, PCCHC*H*), 5.21 (2H, m, PCC*H*CH), 2.56 (3H, d, $^2J_{H-P} = 13.6$ Hz, Me). ^{13}C NMR (CD_2Cl_2, 125 MHz): δ 221.1 (W−*C*O), 135.1 (d, $^4J_{P-C} = 2.1$ Hz, *p*-Ph), 133.6 (d, $J_{P-C} = 10.7$ Hz, Ph), 130.3 (d, $J_{P-C} = 12.9$ Hz, Ph), 121.9 (d, $^1J_{P-C} = 90.3$ Hz, *ipso*-Ph), 91.4 (d, $^2J_{P-C} = 14.0$ Hz, PC*C*HCH), 89.6 (d, $^3J_{P-C} = 11.8$ Hz, PCCHC*H*), 70.5 (d, $^1J_{P-C} = 109.6$ Hz, P*C*), 14.5 (d, $^1J_{P-C} = 65.5$ Hz, Me). ^{31}P NMR (CD_2Cl_2, 121 MHz): δ 18.58. Anal. Found: C, 48.34; H, 3.14. Calcd: C, 47.40; H, 3.22. IR (CH_2Cl_2): 1912, 1808 cm^{-1}.

Synthesis of [(η^5-$C_5H_4PMePh_2$)$Mo(CO)_3I$][I] (VI). A solution of 0.040 g of I_2 (1.6×10^{-4} mol) in 10 mL of CH_2Cl_2 was slowly added to a solution of 0.070 g of **IV** (1.6×10^{-4} mol) in 10 mL of CH_2Cl_2; on addition of the I_2, the yellow solution became bright orange. The reaction mixture was stirred for 30 min and then filtered, and the solvent was removed from the filtrate in vacuo to give 0.059 g of red product (54%). X-ray-quality crystals and analytically pure material were obtained by crystallization from CH_2Cl_2 solution at -30 °C by layering with hexanes. ^1H NMR (CD_2Cl_2, 300 MHz): δ 7.87−7.67 (10H, m, Ph), 6.43 (2H, m, PCCHC*H*), 6.04 (2H, m, PCC*H*CH), 3.12 (3H, d, $^2J_{H-P} = 13.6$ Hz, Me). ^{13}C NMR (CD_2Cl_2, 125 MHz): δ 229.3 (Mo−*C*O), 216.3 (Mo−*C*O), 136.4 (d, $^4J_{P-C} = 3.8$ Hz, *p*-Ph), 133.5 (d, $J_{P-C} = 11.5$ Hz, Ph), 131.2 (d, $J_{P-C} = 13.4$ Hz, Ph), 119.6 (d, $^1J_{P-C} = 91.1$ Hz, *ipso*-Ph), 104.1 (d, $^2J_{P-C} = 11.5$ Hz, PC*C*HCH), 97.5 (d, $^3J_{P-C} = 8.6$ Hz, PCCHC*H*), 87.0 (d, $^1J_{P-C} = 95.0$ Hz, P*C*), 11.7 (d, $^1J_{P-C} = 58.5$ Hz, Me). ^{31}P NMR (CD_2Cl_2, 121 MHz): δ 21.08. Anal. Found: C, 35.58; H, 3.12. Calcd: C, 36.13; H, 2.45. IR (CH_2Cl_2): 2055, 1979 cm^{-1}.

Attempted Reactions of IV with MeI and H_2. To a solution of 0.24 g of **IV** (5.3×10^{-4} mol) in 20 mL of THF was added 0.75 g of MeI (5.3×10^{-4} mol). The solution was stirred for 22 h, with neither color change nor change in the IR spectrum being observed. Similarly, no reaction was observed on bubbling H_2 through a solution of **IV** in THF for 6 h.

Attempted Thermal and Photochemical Reactions of III and IV with PPh_3. Solutions of either **III** or **IV** and 1 equiv of PPh_3 in

Table 1. Selected NMR Data for the Compounds II−VI[a]

position	**II** ($CDCl_3$)	**III** (CD_2Cl_2)	**IV** (CD_2Cl_2)	**V** (CD_2Cl_2)	**VI** (CD_2Cl_2)
			^{1}H NMR		
2, 5	6.29 (m)	4.71 (m)	5.29 (m)	5.21 (m)	6.04 (m)
3, 4	6.44 (m)	4.90 (m)	5.48 (m)	5.46 (m)	6.43 (m)
Me	2.37 (d, $^2J_{P-H} = 13.2$)	2.55 (d, $^2J_{P-H} = 13.2$)	2.55 (d, $^2J_{P-H} = 13.6$)	2.56 (d, $^2J_{P-H} = 13.6$)	3.12 (d, $^2J_{P-H} = 13.6$)
			^{13}C NMR		
1	79.2 (d, $^1J_{P-C} = 114.2$)	65.8 (d, $^1J_{P-C} = 111.4$)	71.8 (d, $^1J_{P-C} = 109.4$)	70.5 (d, $^1J_{P-C} = 109.6$)	87.0 (d, $^1J_{P-C} = 95.0$)
2, 5	114.9 (d, $^2J_{P-C} = 16.3$)	89.9 (d, $^2J_{P-C} = 13.4$)	94.5 (d, $^2J_{P-C} = 14.4$)	91.4 (d, $^2J_{P-C} = 14.0$)	104.1 (d, $^2J_{P-C} = 11.5$)
3, 4	114.3 (d, $^3J_{P-C} = 17.3$)	87.5 (d, $^3J_{P-C} = 13.4$)	92.1 (d, $^3J_{P-C} = 12.5$)	89.6 (d, $^3J_{P-C} = 11.8$)	97.5 (d, $^3J_{P-C} = 8.6$)
Me	12.6 (d, $^1J_{P-C} = 63.3$)	12.8 (d, $^1J_{P-C} = 65.7$)	14.4 (d, $^1J_{P-C} = 66.2$)	14.5 (d, $^1J_{P-C} = 65.5$)	11.7 (d, $^1J_{P-C} = 58.5$)
			^{31}P NMR		
	7.95	19.54	18.25	18.58	21.08

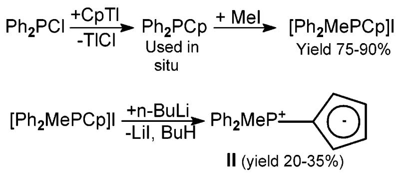
[a] δ values are given in ppm and *J* values in Hz. Full listings of NMR data are given in the Experimental Section. Refer to **A** for the atom-labeling scheme.

20 mL of THF were refluxed for 20 h while being monitored by IR spectroscopy. Similarly, solutions of **IV** and either 1 or 3.5 equiv of PPh_3 in 20 mL of CH_2Cl_2 were photolyzed with UV light from a Hanovia lamp for 20 h, during which time the experiments were monitored by IR. No changes in the IR spectra were observed. A similar photochemical experiment with 1 equiv of PMe_3 had the same result.

Photochemical Reaction of IV with 3.5 Equiv of PMe_3. A solution of **IV** and 3.5 equiv of PMe_3 in 20 mL of CH_2Cl_2 was photolyzed with UV light from a Hanovia lamp while being monitored by IR spectroscopy. After 18 h, the IR spectrum showed that the peaks of **IV** had disappeared and had been replaced by new peaks at 1830 and 1930 cm^{-1}. After removal of the solvent, the residue was dissolved in CD_2Cl_2 and the ^{1}H and ^{31}P NMR spectra were recorded. Free ligand peaks of **II** were observed in both the ^{1}H and ^{31}P NMR spectra, while a new peak in the ^{31}P NMR spectrum corresponds to the resonance of the previously reported complex *fac*-$Mo(PMe_3)_3(CO)_3$ (δ −17 ppm).[11]

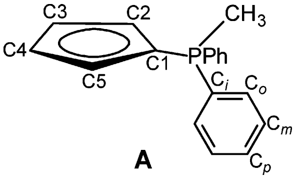
Ab Initio Calculations. To gain information on the electronic structures of $C_5H_4PMePh_2$ (**II**) and (η^5-C_5H_4)$PMePh_2Cr(CO)_3$ (**III**), and also to compare the ylide−metal bonding in **III** with the (η^6-C_6H_6)−metal bonding in (η^6-C_6H_6)$Cr(CO)_3$, a series of ab initio calculations was performed on **II** and **III**, employing the Gaussian 03 suite of programs.[12a] Using the crystal structures as initial starting points, optimized structures were obtained with the B3LYP[12b−d] functional on a self-consistent hybrid-DFT level of calculation in a standard "split valence" 6-31G* basis.[12e−h] Using these structures, we then obtained further results at three levels of computation, B3LYP, restricted Hartee-Fock (RHF), and second-order Møller−Plesset perturbation theory (MP2), as well as in two basis sets, the "split valence" 6-31G* basis, and Dunning's correlation consistent double-ζ basis[12i,j] with the chromium atom represented in a Wachters−Hay basis.[12k,l]

Scheme 1. Synthesis of $C_5H_4PMePh_2$ (II)



Results and Discussion

Synthesis, Structure, and Spectroscopic Properties of II. Ligand **II** was synthesized using a procedure very similar to that of Mathey and Lampin,[9] who had previously reported only its ^{1}H NMR spectrum (Scheme 1). As part of our study, we have now characterized this ligand by ^{1}H, ^{31}P, and ^{13}C{^{1}H} NMR spectroscopy, elemental analyses, and X-ray crystallography. The ^{1}H and ^{13}C{^{1}H} NMR data are presented in Table 1 and will be discussed below. Note that all spectral and structural parameters of free and coordinated cyclopentadienylidenes are presented in terms of the general labeling scheme, shown as **A**. To facilitate comparisons, the atom numbering for the carbon and hydrogen atoms of the C_5H_4 ring corresponds to the crystallographic labeling schemes.



A

The crystal structure of **II** was obtained for purposes of comparison with that of **I**, which was reported previously.[1g] The structure of **II** contains two independent molecules (molecules 1 and 2) in the unit cell (Figure 1), and selected bond lengths and angles for **I** and **II** are given in Table 2. Crystallographic data for **II** and the coordination complexes, prepared here and to be discussed below, are given in Table 3; complete tables of bond lengths and angles may be found in the Supporting Information.

The most important structural parameters for assessing the relative contributions of the resonance structures **IIa** and **IIb**

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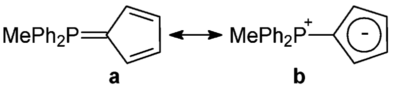
Table 2. Selected Bond Distances and Angles for I and II[a]

	II (molecule 1)	**II** (molecule 2)	**I**[1g]
	Bond Lengths (Å)		
P(1)−C(1)	1.7277(17)	1.7268(17)	1.718(2)
P−Me	1.799(2)	1.7921(19)	
P−Ph (av)	1.810	1.802	1.806
C(1)−C(2)	1.429(3)	1.413(2)	1.430(3)
C(1)−C(5)	1.414(3)	1.429(2)	1.419(3)
C(2)−C(3)	1.374(3)	1.384(2)	1.392(4)
C(4)−C(5)	1.384(3)	1.383(3)	1.376(4)
C(3)−C(4)	1.405(3)	1.407(3)	1.401(4)
	Bond Angles (deg)		
C(1)−P(1)−Me	111.46(9)	111.96(9)	
C(1)−P−Ph (av)	111.44	110.64	111.4
Me−P−Ph (av)	106.96	108.44	
Ph(1)−P(1)−Ph(2)	108.37(8)	106.55(7)	107.5 (av)
C(1)−C(2)−C(3)	107.42(19)	108.36(16)	106.8(2)
C(2)−C(3)−C(4)	108.85(18)	108.16(18)	108.9(2)
C(3)−C(4)−C(5)	108.74(18)	108.87(15)	108.8(2)
C(4)−C(5)−C(1)	107.47(18)	107.50(17)	108.0(2)
C(5)−C(1)−C(2)	107.51(16)	107.11(16)	107.4(2)

[a] Refer to **A** for the atom-labeling scheme.

to the overall electronic structure involve the bond lengths and angles of the P−C_5H_4 moiety. The P−C_5H_4 bond length of **I** is



II

1.718(2) Å,[1g] while those of the two molecules of **II** are 1.7277(17) and 1.7268(17) Å. The slight elongation of the P−C_5H_4 bond distances in **II** may be the result of having substituted a phenyl group for the better donating methyl group, but more to the point, these P−C_5H_4 bonds are all significantly *shorter* than the P−Ph bonds in **I** and **II** (which fall within the typical range for this type of C−P single bond in phenyl phosphonium ylides[13]) but significantly *longer* than the P=CH_2 bond in Ph_3P=CH_2 (1.66 Å).[13] The latter compound is a typical example of a non-resonance-stabilized ylide, and its P=CH_2 bond is believed to contain considerable double-bond character.[13a] Thus, the P−C_5H_4 bond lengths of **I** and **II** are consistent with very significant contribution from both the uncharged and zwitterionic resonance structures **Ia**, **Ib**, **IIa**, **IIb**.

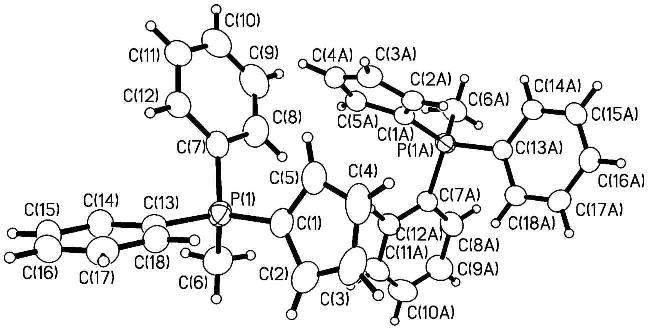


Figure 1. Molecular structures of the two molecules in the unit cell of $C_5H_4PMePh_2$.

Interestingly, although the C−C−C bond angles within the five-membered rings of both ylides are all very close to the 108° of a regular pentagon, the C−C bond lengths seemingly also provide evidence for a degree of localization of π bond electron density. Thus, while the structures of both molecules exhibit long (C_1−C_2), short (C_2−C_3), long (C_3−C_4), short (C_4−C_5), long (C_5−C_1) alternating patterns of bond lengths, as in **Ia** and **IIa**, the "long" bonds are much shorter than a C−C typical single-bond length and all bonds are similar to those of, e.g., benzene (1.3894 Å).[13b] Thus, again there is evidence for a very

Table 3. Crystallographic Data

	II	**III**	**IV**	**V**	**VI**
empirical formula	$C_{18}H_{17}P$	$C_{21}H_{17}CrO_3P$	$C_{21}H_{17}MoO_3P$	$C_{21}H_{17}WO_3P$	$C_{21.50}H_{18}ClI_2MoO_3P$
fw	264.29	400.32	444.26	532.17	740.52
temp (K)	180(2)	180(2)	180(2)	180(2)	180(2)
wavelength (Å)	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
cryst syst	triclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a (Å)	9.2856(8)	9.738(2)	9.6728(7)	9.6818(12)	9.3488(10)
b (Å)	10.8254(9)	14.410(3)	14.5246(10)	14.5322(17)	16.5390(18)
c (Å)	15.0721(13)	13.927(3)	14.1801(10)	14.1153(17)	16.6312(18)
α (deg)	89.602(2)	90	90	90	94.800(2)
β (deg)	83.260(2)	108.742(4)	108.3930(10)	108.514(2)	103.058(2)
γ (deg)	75.6430(10)	90	90	90	90.427(2)
V (Å^3)	1457.2(2)	1850.8(6)	1890.4(2)	1883.2(4)	2495.3(5)
Z	4	4	4	4	4
ρ(calcd) (g/cm^3)	1.205	1.437	1.561	1.877	1.971
μ (mm^{-1})	0.172	0.722	0.795	6.236	3.191
F(000)	560	824	896	1024	1404
cryst size (mm^3)	0.40 × 0.20 × 0.10	0.30 × 0.15 × 0.05	0.30 × 0.15 × 0.08	0.35 × 0.25 × 0.05	0.35 × 0.10 × 0.06
θ range (deg)	2.28−25.00	2.09−25.00	2.06−25.00	2.22−25.00	1.69−25.00
index ranges	$-10 \leq h \leq 11$, $-12 \leq k \leq 11$, $-17 \leq l \leq 17$	$-11 \leq h \leq 10$, $-17 \leq k \leq 15$, $-16 \leq l \leq 16$	$-11 \leq h \leq 11$, $-17 \leq k \leq 17$, $-15 \leq l \leq 16$	$-11 \leq h \leq 11$, $-17 \leq k \leq 16$, $-16 \leq l \leq 16$	$-10 \leq h \leq 11$, $-18 \leq k \leq 19$, $-19 \leq l \leq 19$
no. of rflns collected	8642	10 657	10 967	10 698	14 730
no. of indep rflns	5090 (R(int) = 0.0171)	3263 (R(int) = 0.0373)	3334 (R(int) = 0.0283)	3319 (R(int) = 0.0540)	8747 (R(int) = 0.0384)
completeness to θ = 25.00° (%)	99.50	100	100	99.90	99.40
max, min transmission	1.0000, 0.7520	1.0000, 0.8567	1.0000, 0.8555	0.5984, 0.2118	1.0000, 0.6904
no. of data/restraints/params	5090/0/343	3263/0/235	3334/0/235	3319/0/235	8747/0/532
goodness of fit on F^2	1.000	1.000	1.000	1.000	1.000
final R indices ($I > 2\sigma(I)$)	R1 = 0.0377, wR2 = 0.1015	R1 = 0.0374, wR2 = 0.0672	R1 = 0.0253, wR2 = 0.0470	R1 = 0.0270, wR2 = 0.0849	R1 = 0.0489, wR2 = 0.0996
R indices (all data)	R1 = 0.0509, wR2 = 0.1080	R1 = 0.0613, wR2 = 0.0710	R1 = 0.0381, wR2 = 0.0491	R1 = 0.0295, wR2 = 0.0864	R1 = 0.0832, wR2 = 0.1062
largest diff peak, hole (e Å^{-3})	0.327, −0.299	0.443, −0.355	0.370, −0.267	0.923, −0.796	1.641, −1.349

Scheme 2. Syntheses of (η^5-$C_5H_4PMePh_2$)M(CO)$_3$ (M = Cr, Mo, W)

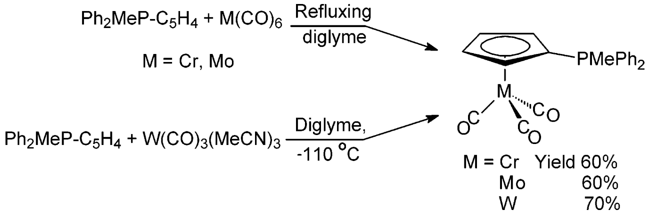


Table 4. Carbonyl Stretching Frequencies for the Compounds III−V (in CH_2Cl_2), for the Neutral Arene Compounds (η^5-C_6H_6)M(CO)$_3$ (M = Cr, Mo, W; in CH_2Cl_2),[14a] and for the Anionic Complexes [(η^5-C_5H_5)M(CO)$_3$]$^-$ (M = Cr, Mo, W; in THF)[14b]

	ν(CO) (cm^{-1})		
M	(η^5-$C_5H_4PMePh_2$)M(CO)$_3$	(η^5-C_6H_6)M(CO)$_3$	[(η^5-C_5H_5)M(CO)$_3$]$^-$
Cr	1915 (s), 1812 (s)	1971, 1892	1895, 1778
Mo	1918 (s), 1812 (s)	1972, 1891	1898, 1781
W	1912 (s), 1808 (s)	1971, 1887	1894, 1779

significant contribution from both the uncharged and the zwitterionic resonance structures of **I** and **II**.

Syntheses, Structures, and Spectroscopic Properties of Group 6 Complexes of II. The group 6 tricarbonyl complexes **III**−**V** were synthesized using procedures similar to those reported by Kotz et al. in the syntheses of the corresponding complexes of **I**.[2b] An excess (2−3 equiv) of M(CO)$_6$ (M = Cr, Mo) was refluxed in diglyme with **II** to give the resulting chromium and molybdenum complexes in ~60% yield for both complexes (Scheme 2); however, the tungsten derivative required the use of W(CO)$_3$(CH$_3$CN)$_3$ to ensure ligand substitution.[2b] An excess of W(CO)$_3$(CH$_3$CN)$_3$ was heated with **II** in diglyme to 110 °C to provide the tungsten complex in 70% yield.

The IR spectra (CH_2Cl_2, Table 4) of the complexes exhibit two strong carbonyl stretching bands, consistent with an essentially 3-fold −M(CO)$_3$ moiety at frequencies nearly identical with those reported for the corresponding complexes of **I**.[2b] For purposes of comparison the ν(CO) values of the analogous η^6-benzene[14a] and anionic η^5-C_5H_5[14b] complexes are also shown in Table 4, and it is clear that the donor properties of **II** lie between those of benzene and Cp$^-$, but possibly closer to the latter. (The data for the Cp$^-$ complexes are believed to be for the free ions, as the spectra were run in the presence of ligands thought to coordinate to the countercations).[14b] These data provide further evidence that the neutral ylides contain significant negative charge on the C_5H_4 rings.

Selected ^{1}H NMR data for **III**−**V** are given in Table 1, where it is shown that coordination of **II** to a metal results in the two multiplet C_5H_4 ring resonances shifting upfield relative to those of the free ligand, while the P−Me ^{1}H resonances shift downfield for the three complexes. Compound **III** shows the greatest change in the C_5H_4 ring proton resonances, which shift upfield by ~1.6 ppm upon complexation of **II**. The C_5H_4 proton resonances for **IV** and **V** exhibit very similar chemical shifts and are downfield of complex **III** by ~0.6 ppm. Similar changes are observed for the group 6 complexes of **I**.[2b]

Table 5. Selected Bond Lengths and Angles of Complexes III−V and (η^5-$C_5H_4PPh_3$)Cr(CO)$_3$[a,2g]

				(η^5-$C_5H_4PPh_3$)Cr(CO)$_3$	
	III	IV	V	molecule 1	molecule 2
		Bond Lengths (Å)			
P(1)−C(1)	1.759(3)	1.759(3)	1.765(4)	1.751(5)	1.755(6)
P−Me	1.789(3)	1.785(2)	1.786(4)		
P−Ph (av)	1.796	1.790	1.793	1.798	1.799
M−C_5 centroid	1.848	2.044	2.033	1.862	1.872
C(1)−C(2)	1.427(4)	1.434(3)	1.435(6)	1.431(8)	1.443(8)
C(1)−C(5)	1.429(4)	1.430(3)	1.438(6)	1.430(8)	1.441(8)
C(2)−C(3)	1.392(4)	1.403(3)	1.405(7)	1.452(9)	1.403(8)
C(4)−C(5)	1.397(4)	1.400(3)	1.393(7)	1.422(9)	1.386(9)
C(3)−C(4)	1.422(4)	1.417(3)	1.402(7)	1.394(10)	1.443(9)
C(1)−metal	2.185(2)	2.350(2)	2.342(4)	2.183(5)	2.192(6)
C(2)−metal	2.204(2)	2.352(2)	2.349(4)	2.201(6)	2.226(6)
C(3)−metal	2.226(3)	2.385(2)	2.371(4)	2.248(7)	2.257(6)
C(4)−metal	2.217(3)	2.403(3)	2.380(5)	2.249(7)	2.238(7)
C(5)−metal	2.191(3)	2.375(2)	2.367(5)	2.229(6)	2.230(6)
		Bond Angles (deg)			
C(1)−P−Me	111.08(13)	110.91(12)	111.2(2)		
C(1)−P−Ph (av)	109.78	109.48	109.19	110.3	109.4
Me−P−Ph (av)	109.38	109.36	109.35		
Ph−P−Ph	107.37(12)	108.35(11)	108.4(2)	108.6	109.7
P−C(1)−C_5 centroid	178.9	178.0	178.5	173.4	169.0
C(1)−C(2)−C(3)	108.3(3)	108.1(2)	107.4(4)	107.4(6)	107.7(6)
C(2)−C(3)−C(4)	108.3(3)	108.1(2)	108.8(4)	108.4(6)	108.3(6)
C(3)−C(4)−C(5)	108.3(3)	108.7(2)	109.1(4)	108.3(6)	108.4(6)
C(4)−C(5)−C(1)	108.0(3)	108.0(2)	107.6(4)	108.8(6)	108.4(6)
C(5)−C(1)−C(2)	107.1(2)	107.1(2)	107.1(4)	107.0(6)	107.2(6)

[a] Refer to **A** for the atom-labeling scheme.

Assignments of the C_5H_4 proton resonances of **II** were made via a NOESY experiment, which showed a strong NOE correlation between the resonance at δ 6.29 and both the Me and the Ph resonances. Thus, the resonance at δ 6.29 is to be assigned to the proton attached to carbon 2,5 (refer to **A** for labeling scheme), since the proton of carbons 3 and 4 would be expected to exhibit much less significant NOE correlations. Carbon assignments were made in part via an HSQC experiment. The resonances of the ipso and para carbons of the phenyl ring were assigned on the basis of their carbon−phosphorus coupling constants, although the corresponding ortho and meta carbon resonances could not be assigned unambiguously because of overlap in the ^{1}H NMR spectrum. Assignment of these by use of the P−C coupling constants was also impossible because of the similarity in magnitudes of the two coupling constants, 10.6 and 11.5 Hz. Where feasible, assignments of the NMR spectra of **III**−**V** were made similarly.

The ^{31}P resonance of **II** shifts downfield some 10−12 ppm on coordination in compounds **III**−**V**, but the differences among the three coordination compounds are relatively small. No spin−spin coupling to ^{183}W was observed in the ^{31}P spectrum of **V**. On the other hand, the ^{13}C NMR spectra exhibit significant changes in the C_5H_4 ring carbon resonances on going from the free ligand to complexes **III**−**V**. Thus, the resonance of C(1) shifts from δ 79.2 in **II** to δ 65.8 ppm in **III**, δ 71.8 in **IV**, and δ 70.5 in **V**, while much more dramatic shifts are observed for the resonances of C(2) and C(3), which shift to higher field by over 20 ppm.

X-ray structures of all three complexes **III**−**V** were obtained; selected bond lengths and angles are given in Table 5 (see the Supporting Information for full listings) and crystallographic data in Table 3. Included in Table 5 are the literature data for (η^5-$C_5H_4PPh_3$)Cr(CO)$_3$, in which there are two independent molecules in the unit cell (molecules 1 and 2).[2g] The structure of (η^5-$C_5H_4PPh_3$)Cr(CO)$_3$ offers a good structural comparison with that of **III** and also allows for a general appraisal of structural changes in this type of ligand on coordination. The molecular structure of **III** is shown in Figure 2; since the crystals of **III**−**V** are all isomorphous, the structures of the latter two

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(13) (a) Bart, J. C. J. *J. Chem. Soc. B* **1969**, 350. (b) Plíva, J.; Johns, J. W. C.; Goodman, L. *J. Mol. Spectrosc.* **1990**, *140*, 214.

(14) (a) Brown, D. A.; Hughes, F. J. *J. Chem. Soc. A* **1968**, 1519. (b) Darensbourg, M. Y.; Jimenez, P.; Sackett, J. R.; Hanckel, J. M.; Kump, R. L. *J. Am. Chem. Soc.* **1982**, *104*, 1521.

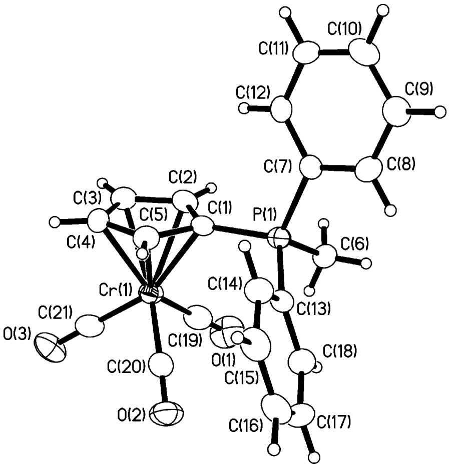
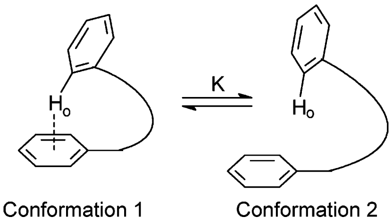


Figure 2. Molecular structure of (η^5-$C_5H_4PMePh_2$)$Cr(CO)_3$.

Scheme 3. Representation of On−Off Equilibrium for Edge−Face Aromatic Ring Interactions



are shown only in the Supporting Information. To our knowledge, the structures of the Mo and W complexes are the first reported crystallographically determined structures for these metals with this class of ligand.

Compounds **III**−**V** all assume near-tetrahedral geometries around the phosphorus atoms, similar to that seen for (η^5-$C_5H_4PPh_3$)$Cr(CO)_3$.[2g] The $C_5H_4PMePh_2$ is coordinated, as expected, in an η^5 fashion in all three complexes, with little difference in the five C_5H_4−Cr distances. The ring carbon atoms C(2) and C(5) essentially eclipse two of the carbonyl ligands, C(19) and C(20), respectively, and thus the third carbonyl ligand assumes a staggered orientation relative to C(3) and C(4). The P−C_5H_4 bond is elongated on coordination to all three metals. The same degree of elongation is observed in (η^5-$C_5H_4PPh_3$)$Cr(CO)_3$[2g] and probably indicates an increase in the contribution of the zwitterionic structure on coordination: i.e., an increase in the aromatic character in the C_5H_4 ring on coordination. The P(1)−C(1)−C_5(centroid) angle is essentially linear in **III**−**V**, the greatest deviation from linearity being ~2.1°. This is in contrast to the case for both free ligands **I** and **II**, for which the P−C_5H_4 bonds are bent significantly out of the C_5H_4 ring planes. The C_5H_4 ring bond lengths of **II** are slightly elongated in **III**−**V**, as is observed in (η^5-$C_5H_4PPh_3$)$Cr(CO)_3$,[2g] and the ring bond angles are all very close to those of a regular pentagon (108°).

The $PMePh_2$ moieties of compounds **II**−**V** are oriented such that one of the phenyl rings not only eclipses the C_5H_4 ring but is oriented toward it in an edge-on fashion in spite of the apparently greater congestion in this conformation. Interestingly, intramolecular edge−face orientations involving interactions of aromatic hydrogen atoms with aromatic π systems have well-established precedent in conformationally flexible compounds, for which equilibria of the type shown generically in Scheme 3 can be established.[15] In these cases, edge−face interactions are sufficiently attractive that the molecules assume Conformation 1 in the solid state, although on−off equilibria exist in solution, as indicated in Scheme 3. Conformation 1 is increasingly populated at lower temperatures, as indicated by significant temperature dependence of the time-averaged chemical shift of the edge hydrogen atom H_o, the observed chemical shift of H_o moving to increasingly higher field as the temperature is lowered because of ring current shielding arising in the close edge−face association of Conformation 1.

The origin of the ring−edge attractive force is believed to be largely electrostatic,[15] the aromatic π electrons interacting with a slightly positive H_o. In view of the apparent significance of resonance structure **IIb** and in accord with DFT calculations to be discussed below, it appears that the C_5H_4 rings of **II** and its coordination complexes are not only aromatic in character but also carry a significant partial negative charge, while the $MePh_2P$− moieties carry a partial positive charge. In addition, for each of the compounds **II**−**V**, the distance between one of the phenyl ortho C−H groups and C(1) of the C_5H_4 ring falls well within the range of distances observed in the previously reported compounds in which attractive edge−face interactions have been established,[15] and one would anticipate relatively strong attractive interactions in compounds **II**−**V**. To seek evidence for the phenomenon in solution, we ran a series of low-temperature ^{1}H NMR experiments with **II** (to 213 K) and **IV** (to 190 K). Unfortunately, no change in the ^{1}H NMR spectrum of either was observed, and thus although edge−face interactions seem to be important in the solid state, no evidence for them has been obtained in solution. However, we note that the apparent electrostatic interactions in compounds **II**−**V** are between phenyl ortho C−H groups and C(1) of the C_5H_4 rings rather than with the *centroids* of the C_5H_4 rings. Thus, it is possible that the ortho hydrogen atoms do not actually lie in the region of ring-current-induced enhanced shielding.

Reactions of IV: Synthesis, Characterization, and Structure of [(η^5-$C_5H_4PMePh_2$)$Mo(CO)_3I$][I]. As part of this study, and to expand on the chemistry of the group 6 tricarbonyl ylide complexes, we have carried out an investigation of the reactivities of **III** and **IV**. Two classes of reactions were studied, ligand substitution and oxidative addition.

We initially began the study of ligand substitution using PPh_3, with a view to substituting CO ligands of **III** and **IV**. To this end, solutions of **III** or **IV** with 1 equiv of PPh_3 were refluxed in THF for up to 22 h while the reactions were monitored by IR spectroscopy. No changes in the IR spectra were apparent after this reaction time. We also attempted photochemical CO substitution reactions of **IV**, but after 18 h of photolyzing a CH_2Cl_2 solution of the metal complex and 1 equiv of phosphine, no change in the IR spectrum was observed. We also attempted CO substitution using PMe_3, anticipating that the use of this smaller, better donor would promote the ligand exchange. As with the PPh_3 experiment, however, no reaction occurred with 1 equiv of PMe_3 after 18 h of photolysis. However, when 3.5 equiv of PMe_3 was used in a photochemical reaction, the ν(CO) band of **IV** disappeared as a new set of peaks in the carbonyl region grew in at 1830 and 1930 cm^{-1}, very similar to the literature values for *fac*-$Mo(CO)_3(PMe_3)_3$.[11] Consistent with this conclusion, ^{1}H and ^{31}P NMR spectra of the crude reaction mixture clearly indicated that the ylide had been cleaved from the metal, and in addition there appeared in the ^{31}P NMR spectrum a new peak at δ −17.2, also attributable to *fac*-$Mo(CO)_3(PMe_3)_3$.[11] The displacement by phosphines of η^6-arenes

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(15) (a) Desiraju, G. R. *Crystal Engineering*; Elsevier: Amsterdam, 1989; pp 92−95. (b) Jennings, W. B.; Farrell, B. M.; Malone, J. F. *Acc. Chem. Res.* **2001**, *34*, 885. (c) Carver, F. J.; Hunter, C. A.; Livingstone, D. J.; McCabe, J. F.; Seward, E. M. *Chem. Eur. J.* **2002**, *8*, 2847. (d) Ercolani, G.; Mencarelli, P. *J. Org. Chem.* **2003**, *68*, 6470.

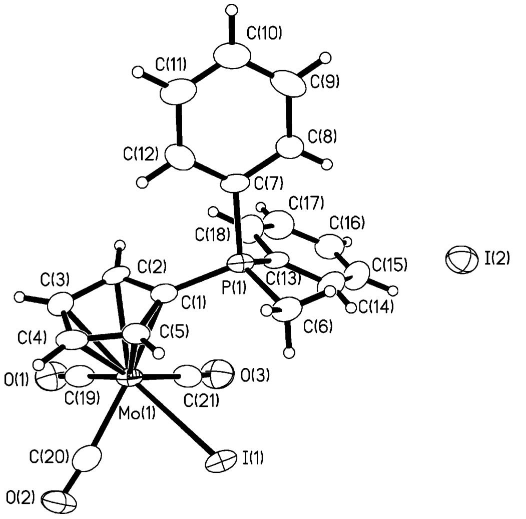

Figure 3. Molecular structure of $[(\eta^5\text{-}C_5H_4PMePh_2)Mo(CO)_3I]I$, showing one of the independent molecules in the unit cell.

of group 6 metal tricarbonyl complexes is known to give *fac* isomers,[11] and we believe this is occurring here. When the photochemical reaction (18 h) was attempted using 3.5 equiv of PPh_3, no reaction occurred. This may be due to the large size of PPh_3 versus that of PMe_3. In general, therefore, **IV** appears to be relatively inert with respect to ligand exchange.

Reactions of the electrophilic reagents I_2, MeI, and H_2 with **IV** were also investigated. The reaction of I_2 with $(\eta^5\text{-}C_5H_4\text{-}PPh_3)Mo(CO)_3$ had been previously reported to give the Mo(II) complex $[(\eta^5\text{-}C_5H_4PPh_3)Mo(CO)_3I][PF_6]$, but only IR and elemental analysis data were reported.[2d] On the addition of 1 equiv of I_2 to a solution of **IV**, the color of the solution changed instantly to orange and, on workup, we isolated the crystalline product $[(\eta^5\text{-}C_5H_4PMePh_2)Mo(CO)_3I]I$. NMR data are given in Table 1 and are consistent with this formulation. As anticipated, the P−Me and C_5H_4 ^1H resonances are all significantly deshielded relative to the precursor, **IV**; the C_5H_4 ring ^{13}C resonances are also significantly deshielded, but not the ^{13}C resonance of the P−Me group. The IR spectrum (CH_2Cl_2 solution) of **VI** exhibited two strong ν(CO) bands at 2055 and 1979 cm^{-1}, as expected at higher frequencies than is the case for **IV** but similar to the reported ν(CO) values for $[(\eta^5\text{-}C_5H_4\text{-}PPh_3)Mo(CO)_3I][PF_6]$ (2052, 1997, and 1976 cm^{-1}; run as a KBr disk).[2d]

Crystals suitable for X-ray crystallography were grown, and the crystal structure of **VI** is shown in Figure 3. Selected bond distances and angles are given in Table 6 (see the Supporting Information for full listings) and crystallographic data in Table 3. The crystal structure contains two independent molecules in the unit cell, molecules 1 and 2, and one molecule of CH_2Cl_2. As with **III**−**V**, the molecules assume piano-stool-type structures about the metal atoms and an ortho hydrogen atom of a phenyl group is positioned relatively closely to C(1) of the C_5H_4 ring. Perhaps because of this, the coordinated iodine atoms are oriented relatively closely to the phosphorus atoms, with the P(1)−C(1)−Mo(1)−I(1) torsional angles being 47.0(5) and 59.7(5)° for molecules 1 and 2, respectively. Observation that the phosphorus atoms are in close proximity to the coordinated iodines seems surprising, but no covalent bonding interaction is present, as the interatomic distances (4.474 and 4.325 Å) exceed the sum of the van der Waals radii.[16] Indeed, the P−C_5H_4 bonds are bent out of the plane of the C_5H_4 ring and away from the metals in the two molecules by ~9.8 and ~7.3°.

Table 6. Selected Bond Lengths and Angles of the Two Molecules of VI[a]

	molecule 1	molecule 2
Bond Lengths (Å)		
P(1)−C(1)	1.780(8)	1.775(9)
P−Me	1.777(8)	1.789(8)
P−Ph (av)	1.792	1.782
M−C_5 centroid	1.997	1.994
C(1)−C(2)	1.436(10)	1.437(11)
C(1)−C(5)	1.440(10)	1.412(11)
C(2)−C(3)	1.428(11)	1.418(12)
C(4)−C(5)	1.385(11)	1.415(11)
C(3)−C(4)	1.401(11)	1.386(12)
Mo−I(1)	2.8355(9)	2.8176(10)
C(1)−Mo	2.310(7)	2.318(8)
C(2)−Mo	2.301(8)	2.292(8)
C(3)−Mo	2.324(8)	2.312(8)
C(4)−Mo	2.360(8)	2.361(9)
C(5)−Mo	2.370(8)	2.356(8)
Bond Angles (deg)		
C(1)−P−Me	108.1(4)	108.5(4)
C(1)−P−Ph (av)	110.8	109.6
Me−P−Ph (av)	110.0	111.0
Ph−P−Ph	106.9(4)	107.1(4)
P−C(1)−C_5 centroid	170.2	172.7
C(1)−C(2)−C(3)	107.0(8)	108.1(8)
C(2)−C(3)−C(4)	108.1(7)	108.3(8)
C(3)−C(4)−C(5)	109.7(8)	108.5(8)
C(4)−C(5)−C(1)	107.9(7)	108.9(8)
C(5)−C(1)−C(2)	107.2(7)	106.2(8)

[a] Refer to **A** for the atom-labeling scheme.

The P−C_5H_4 bond lengths of the two molecules of **VI** are slightly longer (1.780(8), 1.775(9) Å) than is the case with **IV** (1.759(2) Å), while the C−C distances in the C_5H_4 ring lose the alternating bond lengths found in **II** and **IV**. Both of these factors are consistent with an increase in aromatic character in the C_5H_4 ring on oxidation of the metal. The metal−C_5H_4 ring centroid distance decreases (1.997 and 1.994 Å) on oxidation, as is to be expected, but the individual Mo−C bond distances vary somewhat irregularly, with the distances to C(4) and C(5) being somewhat longer than those to C(1), C(2) and C(3).

Reaction of **IV** with MeI was attempted as a test of nucleophilicity of **IV**. The analogous $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]^-$ reacts readily with MeI to give $(\eta^5\text{-}C_5H_5)Mo(CO)_3Me$,[17] but **IV** was found to be inert to MeI. There was also no reaction of **IV** with H_2.

Electronic Structures of $C_5H_4PMePh_2$ (II) and $(\eta^5\text{-}C_5H_4)\text{-}PMePh_2Cr(CO)_3$ (III). Geometry optimizations of **II** and **III** were carried out using B3LYP[12b−d] in a 6-31G* basis set.[12e−h] The geometries obtained in this way were kept fixed in all subsequent computations. Bond lengths and angles obtained in the DFT-optimized structures for $C_5H_4PMePh_2$ (**II**) and $(\eta^5\text{-}C_5H_4)PMePh_2Cr(CO)_3$ (**III**) are shown in Table 7, together with the crystallographic data for **II** and **III**. As can be seen, the calculated bond lengths and angles are generally in reasonable agreement with the experimental data for both the free and coordinated ylide ligand, and in particular the same *trends* are observed. Thus, the P(1)−C(1) bonds of both compounds are calculated to be significantly shorter than the averages of the P−phenyl bonds, consistent with the calculated partial double-bond character in the former; the Mulliken−Mayer bond index for the P(1)−C(1) bond is about 1.2, as opposed to 0.9 for the P−phenyl bonds. In addition, the experimentally observed lengthening of the P(1)−C(1) bond on coordination is also

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(16) Emsley, J. *The Elements*, 2nd ed.; Clarendon Press: Oxford, U.K., 1991.

(17) Jolly, W. L. *Inorg. Synth.* **1968**, *11*, 116.

Table 7. Calculated (6-31G* B3LYP) and Experimental Bond Lengths and Angles of $C_5H_4PMePh_2$ (II) and of (η^5-$C_5H_4PMePh_2$)$Cr(CO)_3$ (III)[a]

	II		III	
	exptl	calcd	exptl	calcd
	Bond Lengths (Å)			
P(1)−C(1)	1.7277(17), 1.7268(17)	1.717	1.759(3)	1.757
P−Me	1.799(2), 1.7921(19)	1.835	1.789(3)	1.825
P−Ph (av)	1.810, 1.802	1.836	1.796	1.822
C(1)−C(2)	1.429(3), 1.413(2)	1.439	1.427(4)	1.449
C(1)−C(5)	1.414(3), 1.429(2)	1.441	1.429(4)	1.443
C(2)−C(3)	1.374(3), 1.384(2)	1.387	1.392(4)	1.409
C(4)−C(5)	1.384(3), 1.383(3)	1.388	1.397(4)	1.413
C(3)−C(4)	1.405(3), 1.407(3)	1.426	1.422(4)	1.430
	Bond Angles (deg)			
C(1)−P(1)−Me	111.46(9), 111.96(9)	110.47	111.08(13)	110.14
C(1)−P−Ph (av)	111.44, 110.64	113.29	109.78	111.95
Me−P−Ph (av)	106.96, 108.44	106.17	109.38	107.45
Ph−P−Ph	108.37(8), 106.55(7)	106.97	107.37(12)	107.64
C(1)−C(2)−C(3)	107.42(19), 108.36(16)	107.36	108.3(3)	107.6
C(2)−C(3)−C(4)	108.85(18), 108.16(18)	108.88	108.3(3)	109.0
C(3)−C(4)−C(5)	108.74(18), 108.87(15)	108.89	108.3(3)	108.2
C(4)−C(5)−C(1)	107.47(18), 107.50(17)	107.24	108.0(3)	108.1
C(5)−C(1)−C(2)	107.51(16), 107.11(16)	107.61	107.1(2)	107.2

[a] Refer to **A** for the atom-labeling scheme.

reflected in the calculations. The alternating bond lengths of the C_5H_4 rings of both free and coordinated ylide, noted above, are also reproduced in the calculated geometries, as well as in the bond indices (typically 1.2 for long and 1.5 for short bonds). This finding lends further credence to our conclusion of significant delocalization of the π system of the C_5H_4 rings.

The Mulliken charges for the free ligand **II** were computed at the B3LYP, RHF, and MP2 levels of computation, both in the Pople split-valence (6-31G*) and the Dunning double-ζ (cc-pVDZ) basis sets. While the charges calculated for individual atoms are very basis set dependent, they become more consistent if the hydrogen atoms are combined with the heavy atoms to which they are bound, and even more so if one looks only at the overall groups (C_5H_4 ring, phenyl rings, methyl). In this case we find that the C_5H_4 ring of the free ligand carries a charge of about −0.5 independent of the type of calculation, the phenyl rings and the methyl group are near neutral, and the charge on phosphorus is between +0.4 and +0.7, depending on the level and basis set. Somewhat similar results have been reported recently for **I**.[1i]

In the case of the chromium complex **III**, calculations based on all of the basis sets suggest that the C_5H_4 ring is less negative than is the case in the free ligand, as anticipated, and that the overall charge of the $Cr(CO)_3$ group is negative, with the negative charge largely delocalized onto the CO ligands. Again the phosphorus atom carries a positive charge, while the methyl and phenyl groups are essentially neutral.

We have also calculated the ylide−$Cr(CO)_3$ bond dissociation energy and have compared this with the analogous ring−metal bond dissociation energy of (η^6-C_6H_6)$Cr(CO)_3$.[18] The calculations were based on the B3LYP/6-31G* gas-phase geometries: i.e., without reoptimization. Values of the calculated ylide−$Cr(CO)_3$ and C_6H_6−$Cr(CO)_3$ bond dissociation energies varied considerably, being consistently greater for MP2 than for Hartree−Fock, as well as greater for the smaller basis set. Interestingly, however, the ratio of the ylide−$Cr(CO)_3$ to the C_6H_6−$Cr(CO)_3$ bond dissociation energy was consistently about 1.3, and thus the ylide−$Cr(CO)_3$ bond dissociation energy appears to be about 30% stronger than the C_6H_6−$Cr(CO)_3$ bond dissociation energy.

Contour plots of the HOMO and HOMO-1 of free $C_5H_4PMePh_2$ are shown in Figure 4A,B, respectively. These differ by only 6 kcal/mol and, as can be seen, correspond closely to the doubly degenerate HOMO (E_1 symmetry) of the free (D_{5h}) cyclopentadienyl anion.[19] That they are not degenerate reflects

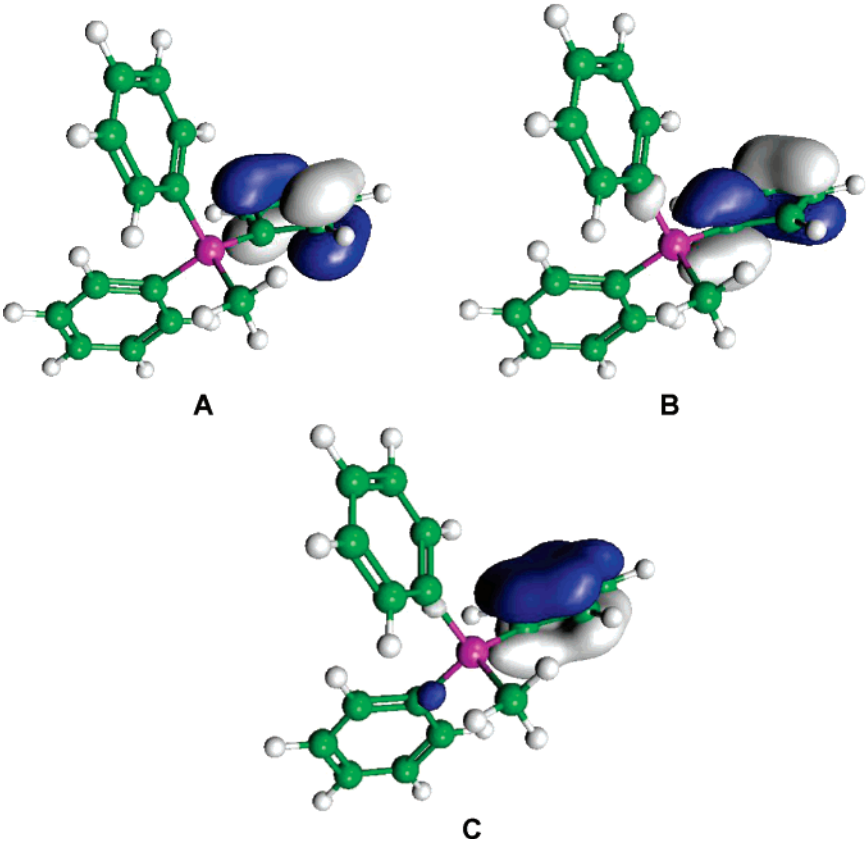

Figure 4. Contour plots of the HOMO (A), HOMO-1 (B), and HOMO-6 (C) of free $C_5H_4PMePh_2$. The contour values are ±0.05.

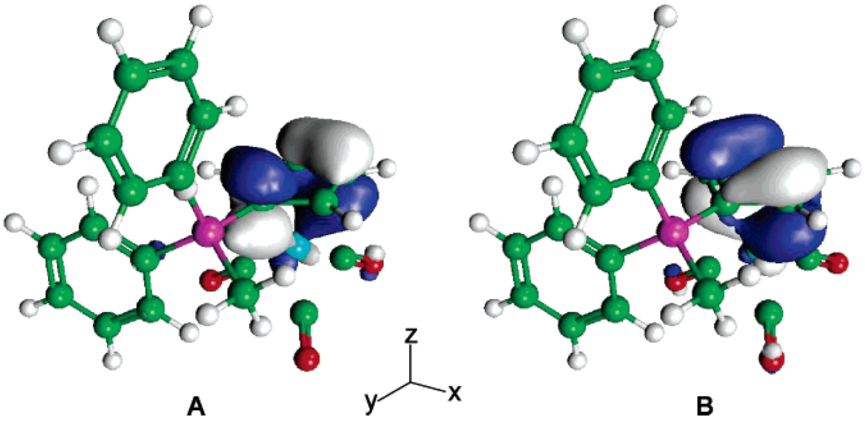

Figure 5. Contour plots of the primary η^5-C_5H_4−Cr interactions in (η^5-$C_5H_4PMePh_2$)Cr(CO)$_3$, involving the d_{xz} (A, HOMO-4) and d_{yz} (B, HOMO-3) orbitals on Cr. The contour values are ±0.05.

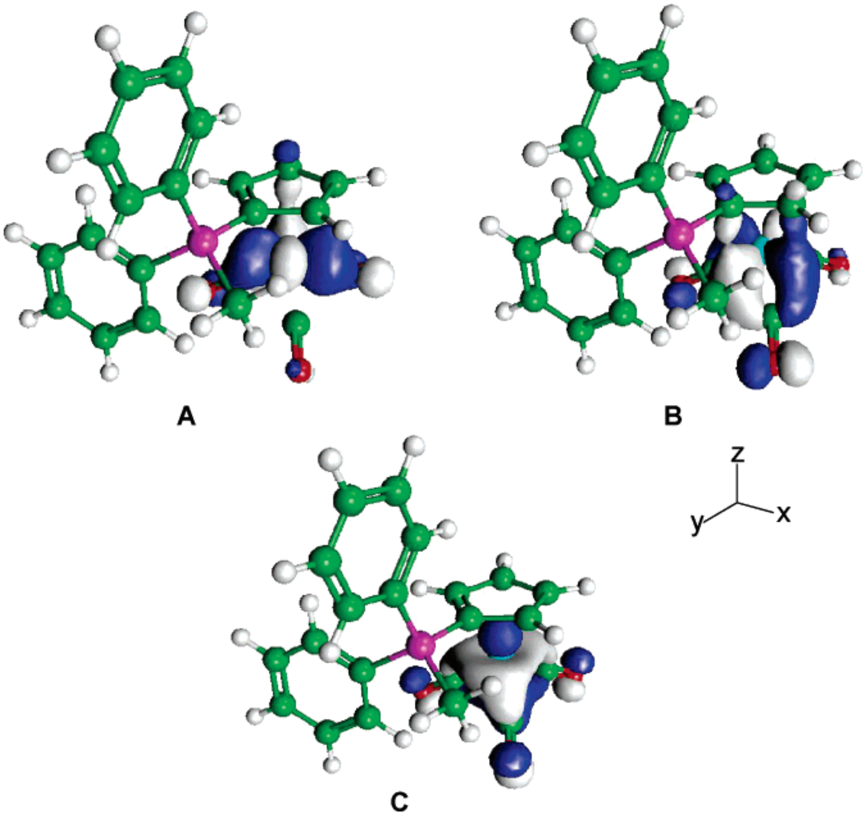

Figure 6. Contour plots showing the interactions between the CO ligands and the d orbitals of (η^5-$C_5H_4PMePh_2$)Cr(CO)$_3$: (A) the $d_{x^2-y^2}$ orbital (HOMO); (B) the d_{xy} orbital (HOMO-1); (C) the d_{z^2} orbital (HOMO-2). The contour values are ±0.05.

the lack of symmetry in the molecule. The LUMO and LUMO+1, as well as HOMO-2 to HOMO-5 of free C_5H_4-$PMePh_2$, are all essentially localized on the phenyl rings and hence are not of interest here. However, Figure 4C shows the HOMO-6 orbital, which is the low-energy, almost fully symmetric bonding MO of the C_5H_4 ring, corresponding to the fully symmetric bonding A_1 MO of the cyclopentadienyl anion.[19] Interestingly, there appears to be little π-type interaction of any of the orbitals shown in Figure 4 with an orbital on the phosphorus atom, consistent with a lack of significant π conjugation of the phosphorus atom with the C_5H_4 ring and suggesting that the zwitterionic resonance structure **IIb** may well be the better representation of the electronic structure of **II**.

As with cyclopentadienyl complexes,[19b] the primary η^5-C_5H_4−Cr interaction involves donation from the near-degenerate, filled orbitals shown in Figure 4A,B into the appropriate d orbitals of the metal. If Cartesian axes are chosen as in Figure 5, then the receptor orbitals are the d_{xz} and d_{yz} orbitals, as shown in the contour plots of parts A and B of Figure 5, respectively. Orbitals of (η^5-$C_5H_4PMePh_2$)Cr(CO)$_3$ which are largely $d_{x^2-y^2}$ (HOMO), d_{xy} (HOMO-1), and d_{z^2} (HOMO-2) in character but which contribute to bonding with the CO ligands are shown in parts A−C of Figure 6, respectively.

Summary. Methyldiphenylphosphonium cyclopentadienylide, $C_5H_4PMePh_2$ (**II**), has been synthesized and characterized spectroscopically (^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR) and crystallographically, and its electronic structure has been investigated via ab initio methodologies. The best representation of **II** appears to be the zwitterionic structure **IIb**, and it is found that the HOMO and HOMO-1 orbitals of **II** are near-degenerate and exhibit symmetries very similar to those of the corresponding, doubly degenerate HOMO (E_1 symmetry) of the free (D_{5h}) cyclopentadienyl anion. There is also, at a lower energy, an almost fully symmetric orbital which corresponds to the fully symmetric bonding A_1 MO of the cyclopentadienyl anion. In none of these three orbitals do there appear to be significant π interactions with an orbital on the phosphorus atom, again consistent with the zwitterionic resonance structure **IIb**. Observations that **II** forms the stable coordination compounds (η^5-$C_5H_4PMePh_2$)M(CO)$_3$ (M = Cr, Mo, W) also demonstrate that the implied aromatic cyclopentadienyl anion-like structure is of major significance. The three group 6 metal complexes have been investigated by spectroscopy (IR and ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR), crystallography, and ab initio calculations. In all cases the metal−carbon bond distances are very similar, consistent with a cyclopentadienyl-like structure, while comparisons of ν(CO) values of the complexes (η^5-$C_5H_4PMePh_2$)M(CO)$_3$ (M = Cr, Mo, W) with those of the isoelectronic complexes (η^6-C_6H_6)M(CO)$_3$ and [(η^5-C_5H_5)M(CO)$_3$]$^-$ suggest that the electron-donating ability of the ylide is less than that of the cyclopentadienyl anion but much greater than that of benzene. The primary bonding interaction of the ylide with the Cr(CO)$_3$ moiety involves donation of the HOMO and HOMO-1 orbitals into the metal d_{xz} and d_{yz} orbitals, and the calculated ylide−Cr(CO)$_3$ bond dissociation energy is about 30% higher than the analogous ring−metal bond dissociation energy of (η^6-C_6H_6)Cr(CO)$_3$.

Aspects of the chemistry of the compounds (η^5-C_5H_4-$PMePh_2$)M(CO)$_3$ (M = Cr, Mo) have been investigated. Thermal and photochemical substitution of the CO ligands by equimolar amounts of PMe_3 and PPh_3 was not observed, but the ylide is displaced photochemically from (η^5-$C_5H_4PMePh_2$)-Mo(CO)$_3$ by excess PMe_3 to form *fac*-Mo(CO)$_3$(PMe_3)$_3$. The compound (η^5-$C_5H_4PMePh_2$)Mo(CO)$_3$ does not react with MeI or H_2, but it does react with I_2 to form [(η^5-$C_5H_4PMePh_2$)Mo(CO)$_3$I]I, which has been characterized spectroscopically (IR, ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR) and crystallographically. An interesting and unanticipated feature of the crystal structures of the free ylide and all four of its coordination complexes is that one of the ylide phenyl rings not only eclipses the C_5H_4 ring but also is oriented toward it in an edge-on fashion. The intramolecular edge−face orientations involve interactions of one aromatic hydrogen atom with the C_5H_4 aromatic π systems and are rationalized in terms of electrostatic attractive forces between the slightly positive phenyl hydrogen atom and the negatively charged C_5H_4 ring.

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Supporting Information Available: Crystallographic details, including figures of $C_5H_4PMePh_2$, (η^5-$C_5H_4PMePh_2$)Cr(CO)$_3$, (η^5-$C_5H_4PMePh_2$)Mo(CO)$_3$, (η^5-$C_5H_4PMePh_2$)W(CO)$_3$ and [(η^5-C_5H_4-$PMePh_2$)Mo(CO)$_3$I]I, showing complete numbering schemes and thermal ellipsoid figures, tables of positional and thermal parameters and bond lengths and angles, and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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