



## Note

# Synthesis, properties and structures of methyldiphenylphosphonium 1-indenylide, 1-C<sub>9</sub>H<sub>6</sub>PMePh<sub>2</sub>, and its chiral tricarbonylchromium(0) complex Cr(η<sup>5</sup>-1-C<sub>9</sub>H<sub>6</sub>PMePh<sub>2</sub>)(CO)<sub>3</sub>

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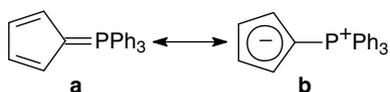
## ABSTRACT

The hitherto unknown indenyl-derived ylide, methyldiphenylphosphonium 1-indenylide, 1-C<sub>9</sub>H<sub>6</sub>PMePh<sub>2</sub> (**1**) and its chromium(0) complex, Cr(η<sup>5</sup>-1-C<sub>9</sub>H<sub>6</sub>PMePh<sub>2</sub>)(CO)<sub>3</sub> (**2**) have been synthesized and characterized spectroscopically and crystallographically. The structures and properties of **1** and **2** are compared with those of the analogous C<sub>5</sub>H<sub>4</sub>PMePh<sub>2</sub> and its chromium complex, Cr(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>PMePh<sub>2</sub>)(CO)<sub>3</sub>. Compound **2**, obtained as a racemic mixture, exhibits planar chirality resulting from coordination of the prochiral aromatic ligand.

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## 1. Introduction

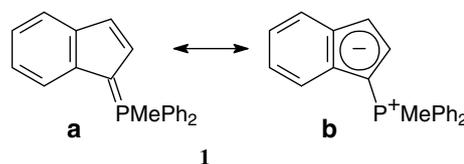
We have recently reported on the synthesis and reactivity of the group 6 compounds M(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>PMePh<sub>2</sub>)(CO)<sub>3</sub> (M = Cr, Mo, W), containing the ligand methyldiphenylphosphonium cyclopentadienylide, C<sub>5</sub>H<sub>4</sub>PMePh<sub>2</sub> [**1**]. This ligand belongs to a class of phosphonium cyclopentadienylides that were first reported in 1956 by Ramirez and Levy [**2a**] who synthesized triphenylphosphonium cyclopentadienylidene, C<sub>5</sub>H<sub>4</sub>PPh<sub>3</sub> [**2b–f**]. They found *inter alia* that this ylide is unusually inert; unlike normal ylides, it does not react with ketones. They attributed this unusual stability to the electron delocalization implied by resonance structure **b**, consistent with the relatively high dipole moment of 7.0 D [**2c**].



Further evidence for extensive delocalization of the π electron density was found in the crystal structure, which showed significant shortening of the P–C<sub>5</sub>H<sub>4</sub> bond [**2g**], and in the <sup>13</sup>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 [**2h**]. Our recent report [**1**] has shown that C<sub>5</sub>H<sub>4</sub>PMePh<sub>2</sub> has properties similar to those of C<sub>5</sub>H<sub>4</sub>PPh<sub>3</sub>.

One of the notable problems that may have limited the exploration of this class of ligand is the lack of a general synthetic route, since the original Ramirez synthetic procedure [**2**] appears not to be generally applicable to other phosphine systems [**3**]. In an attempt to extend the chemistry of this class of ligand, we have begun an investigation into the use of the indenyl-derived ylide, methyldiphenylphosphonium 1-indenylide, 1-C<sub>9</sub>H<sub>6</sub>PMePh<sub>2</sub> (**1**).



The first indenyl-derived phosphorus ylide, triphenylphosphonium 1-indenylide (1-C<sub>9</sub>H<sub>6</sub>PPh<sub>3</sub>), was reported by Crofts and Williams in 1967 [**4**] while Rufanov et al. reported the synthesis of two other phosphonium 1-indenylides, 1-C<sub>9</sub>H<sub>6</sub>P(CH<sub>2</sub>Ph)Ph<sub>2</sub> and 1-C<sub>9</sub>H<sub>6</sub>P(CH<sub>2</sub>C<sub>6</sub>F<sub>5</sub>)Ph<sub>2</sub>, in 2004 [**5**]. However the chemistry of these three potentially very interesting aromatic ligands has been little investigated and, indeed, to our knowledge no other indenyl-derived ylides have been reported. Furthermore, although

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aromatic ligands of the type  $1\text{-C}_9\text{H}_6\text{PR}_3$  are prochiral with the result that their coordination compounds would exhibit planar chirality, no transition metal complexes of any indenyl-derived ylide appear to have been reported. We therefore describe herein the synthesis and characterization of the new ligand, methylidiphenylphosphonium 1-indenylidene,  $1\text{-C}_9\text{H}_6\text{PMePh}_2$  (**1**) and of its chiral chromium complex,  $\text{Cr}(\eta^5\text{-}1\text{-C}_9\text{H}_6\text{PMePh}_2)(\text{CO})_3$  (**2**).

## 2. Experimental

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 Schlenk techniques and an MBraun Labmaster glove box. NMR spectra were recorded using Bruker AV 300, AV 500 and AV 600 spectrometers, all  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra being referenced to carbons or residual protons present in the deuterated solvents with respect to TMS at  $\delta$  0.  $^{31}\text{P}$  NMR spectra were referenced to external 85%  $\text{H}_3\text{PO}_4$ . IR spectra were acquired on a Perkin Elmer Spectrum One FT-IR spectrometer at a spectral resolution of  $4\text{ cm}^{-1}$ . Elemental analyses were conducted by Canadian Microanalytical Service Ltd. of Delta, BC.

Anhydrous dichloromethane, tetrahydrofuran, ethyl 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). The THF,  $\text{Et}_2\text{O}$  and  $\text{CH}_2\text{Cl}_2$  acquired in this way were also subsequently stored over 4A molecular sieves to result in residual water concentrations that were lower than 20 ppm (Karl Fischer titrations). NMR solvents used for organometallic compounds were degassed under vacuum and dried by passage through a small column of activated alumina and storage 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. 1-Diphenylphosphinoindene, as a mixture of 1-diphenylphosphinoind-2-ene and 1-diphenylphosphinoind-1-ene, was synthesized according to a literature procedure [6a].

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 collections were performed on a Bruker smart CCD 1000 X-ray diffractometer with graphite-monochromated  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073\text{ \AA}$ ) controlled with 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 [7a]. Neutral atom scattering factors were taken from Cromer and Waber [7b]. The raw intensity data were converted (including corrections for scan speed, background and Lorentz and polarization effects) to structure amplitudes and their esds using the program SAINT, which corrects for  $L_p$  and decay. Absorption corrections were applied using the program SADABS. All non-hydrogen atoms were refined anisotropically. The positions for all hydrogen atoms were calculated (unless otherwise stated) and their contributions were included in the structure factors and calculations.

For **2**, difference electron density maps revealed the presence of disordered lattice solvate molecules, which were ultimately accounted for through the use of the SQUEEZE subroutine of the PLATON software suite [7c]. Two solvent accessible voids per lattice were found, comprising an equal volume of  $203.1\text{ \AA}^3$  and contributing a total of 38.8 electrons. The voids were thus assigned to two dis-

ordered  $\text{CH}_2\text{Cl}_2$  molecules. Each  $\text{CH}_2\text{Cl}_2$  has 42 electrons, and occupies about  $60\text{ \AA}^3$  in space theoretically. The larger volume of the void in the crystal may be a result of the disorder. The contributions have been included in all derived crystal quantities although the precise composition of the lattice solvate is somewhat speculative.

### 2.1. Synthesis of $[1\text{-C}_9\text{H}_7\text{PMePh}_2]\text{I}$

A solution of 5.1 g  $1\text{-C}_9\text{H}_7\text{PPh}_2$  (as a mixture of isomers) [6a] ( $1.7 \times 10^{-2}\text{ mol}$ ) in 20 mL of THF was treated with 1.0 mL MeI ( $1.6 \times 10^{-2}\text{ mol}$ ), and the reaction mixture was stirred for 2 days while a white precipitate slowly formed. The resulting solid was filtered, washed with ether ( $3 \times 10\text{ mL}$ ) and dried under reduced pressure to give 5.6 g of white  $[1\text{-C}_9\text{H}_7\text{PMePh}_2]\text{I}$  (75% yield).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  8.10–6.90 (m, Ph, possibly olefinic), 6.7–6.15 (m, olefinic), 3.18 (d,  $^2J_{\text{P-H}} = 13.3\text{ Hz}$ , PMe), 2.85 (d,  $^2J_{\text{P-H}} = 13.3\text{ Hz}$ , PMe).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 121 MHz):  $\delta$  26.04, 13.52.

### 2.2. Synthesis of $1\text{-C}_9\text{H}_6\text{PMePh}_2$ (**1**)

A mixture of 1.30 g  $[1\text{-C}_9\text{H}_7\text{PMePh}_2]\text{I}$  ( $2.94 \times 10^{-3}\text{ mol}$ ) and 0.126 g NaH ( $5.25 \times 10^{-3}\text{ mol}$ ) in 20 mL of THF was stirred for 4 days and then filtered. The solid residue was washed  $3 \times 5\text{ mL}$  of THF, and the combined solutions were concentrated to  $\sim 20\text{ mL}$  and then layered with 50 mL of hexanes and cooled to  $-30\text{ }^\circ\text{C}$  to give a light green solid. This was filtered, washed with  $3 \times 20\text{ mL}$  of hexanes, redissolved in 20 mL of  $\text{CHCl}_3$  and then taken to dryness under reduced pressure again to yield 0.80 g (87%) of a green solid that was used without further purification. X-ray quality crystals and analytically pure **1** were obtained by crystallization from a  $\text{CH}_2\text{Cl}_2$  solution layered with hexanes and kept at  $-30\text{ }^\circ\text{C}$ .  $^1\text{H}$  and  $^{13}\text{C}$  NMR data are listed in Table 1.  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 121 MHz):  $\delta$  5.69. Anal. Calc. for  $\text{C}_{22}\text{H}_{19}\text{P}$ : C, 84.06; H, 6.09. Found: C, 84.38; H, 6.35%.

### 2.3. Synthesis of $\text{Cr}(\eta^5\text{-}1\text{-C}_9\text{H}_6\text{PMePh}_2)(\text{CO})_3$ (**2**)

A solution of 0.435 g **1** ( $1.38 \times 10^{-3}\text{ mol}$ ) and 0.692 g  $\text{Cr}(\text{CO})_6$  ( $3.46 \times 10^{-3}\text{ mol}$ ) in 25 mL diglyme was refluxed for 3 h before being cooled and filtered through Celite. The Celite was washed with  $3 \times 10\text{ mL}$  of diglyme, and the resulting orange-red solution was combined with 175 mL of hexanes to give a red-brown solid which was collected and redissolved in  $\sim 15\text{ mL}$  of  $\text{CH}_2\text{Cl}_2$ . Addition of 40 mL of hexanes and cooling of this solution to  $-30\text{ }^\circ\text{C}$  resulted in the precipitation of 0.25 g of orange-brown product (40% yield). Analytically pure, X-ray quality crystals of **2** were obtained by recrystallization from a  $\text{CH}_2\text{Cl}_2$  solution layered with hexanes at  $-30\text{ }^\circ\text{C}$ . IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu(\text{CO})$  1916 (s), 1816 (s), 1802 (sh)  $\text{cm}^{-1}$ .  $^1\text{H}$  and  $^{13}\text{C}$  NMR data are listed in Table 2.  $^{31}\text{P}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 121 MHz):  $\delta$  19.84. Anal. Calc. for  $\text{C}_{25}\text{H}_{19}\text{Cr}_1\text{O}_3\text{P}_1 \cdot 0.5\text{CH}_2\text{Cl}_2$ : C, 62.14; H, 4.09. Found: C, 61.90; H, 4.04%.

## 3. Results and discussion

### 3.1. Syntheses of $1\text{-C}_9\text{H}_6\text{PMePh}_2$ (**1**) and $\text{Cr}(\eta^5\text{-}1\text{-C}_9\text{H}_6\text{PMePh}_2)(\text{CO})_3$ (**2**)

Compound **1** was synthesized using a protocol very similar to that used previously by Mathey et al. [8] and ourselves [1] to obtain  $\text{C}_5\text{H}_4\text{PMePh}_2$ . The precursor, 1-diphenylphosphinoindene, was alkylated with MeI to give the corresponding phosphonium salt  $[1\text{-C}_9\text{H}_7\text{PMePh}_2]\text{I}$  (75% yield) as a mixture of the two isomers shown in Scheme 1 [6a]. The  $^1\text{H}$  NMR spectrum of the phosphonium salt is very complicated in the olefinic region and exhibits

**Table 1**  
<sup>1</sup>H and <sup>13</sup>C NMR data for **1**

Position	$\delta$ ( <sup>1</sup> H) <sup>a</sup>	Multiplicity	<i>J</i> (Hz)	$\delta$ ( <sup>13</sup> C)	Multiplicity	<i>J</i> (Hz)
1				66.14	d	<sup>1</sup> <i>J</i> <sub>P-C</sub> = 120.8
2	6.74	t	<i>J</i> <sub>H-H</sub> = <i>J</i> <sub>P-H</sub> = 4.5	126.30	d	<sup>2</sup> <i>J</i> <sub>P-C</sub> = 17.6
3	6.64	t	<i>J</i> <sub>H-H</sub> = <i>J</i> <sub>P-H</sub> = 4.2	105.00	d	<sup>3</sup> <i>J</i> <sub>P-C</sub> = 15.4
4	7.68	m		120.82	s	
5	6.97	t	<sup>3</sup> <i>J</i> <sub>H-H</sub> = 7.2	117.28	s	
6	6.84	t	<sup>3</sup> <i>J</i> <sub>H-H</sub> = 6.8	117.91	s	
7	7.04	d	<sup>3</sup> <i>J</i> <sub>H-H</sub> = 7.9	117.36	s	
8				137.79	d	<sup>3</sup> <i>J</i> <sub>P-C</sub> = 15.4
9				135.42	d	<sup>2</sup> <i>J</i> <sub>P-C</sub> = 14.3
10	2.5	d	<sup>2</sup> <i>J</i> <sub>P-H</sub> = 12.6	12.97	d	<sup>1</sup> <i>J</i> <sub>P-C</sub> = 62.6
11				127.13	d	<sup>1</sup> <i>J</i> <sub>P-C</sub> = 87.8
12	7.55–7.52	m		129.45	d	<sup>2</sup> <i>J</i> <sub>P-C</sub> = 12.1
13	7.67–7.63	m		132.68	d	<sup>3</sup> <i>J</i> <sub>P-C</sub> = 11.0
14	7.67–7.53	m		132.93	d	<sup>4</sup> <i>J</i> <sub>P-C</sub> = 3.3

<sup>a</sup> The proton correspond to the proton attached to the carbon atom with the same position number in Fig. 2.

**Table 2**  
<sup>1</sup>H and <sup>13</sup>C NMR data for **2**

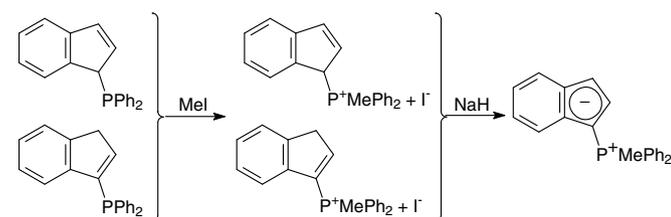
Position	$\delta$ ( <sup>1</sup> H) <sup>a</sup>	Multiplicity	<i>J</i> (Hz)	$\delta$ ( <sup>13</sup> C)	Multiplicity	<i>J</i> (Hz)
1				57.2	d	<sup>1</sup> <i>J</i> <sub>P-C</sub> 113.8
2	4.76	m	<sup>3</sup> <i>J</i> <sub>H-H</sub> 3.0	95.68	d	<sup>2</sup> <i>J</i> <sub>P-C</sub> 13.9
3	5.47	m	<sup>3</sup> <i>J</i> <sub>H-H</sub> 3.0	80.31	d	<sup>3</sup> <i>J</i> <sub>P-C</sub> 12.5
4	7.66	m		127.53	s	
5	7.00	td	<sup>3</sup> <i>J</i> <sub>H-H</sub> 7.6 <sup>4</sup> <i>J</i> <sub>H-H</sub> 1.5	123.28	s	
6	6.92	t*	<sup>3</sup> <i>J</i> <sub>H-H</sub> 8.7	122.16	s	
7	6.90	d*	<sup>3</sup> <i>J</i> <sub>H-H</sub> 7.6	124.60	s	
8,9				109.80	d	<i>J</i> <sub>P-C</sub> 16.6
				109.72	d	<i>J</i> <sub>P-C</sub> 16.6
10	2.88	d	<sup>2</sup> <i>J</i> <sub>P-H</sub> 13.2	14.68	d	<sup>1</sup> <i>J</i> <sub>P-C</sub> 65.2
11				123.10	d	<sup>1</sup> <i>J</i> <sub>P-C</sub> 87.4
				122.43	d	<sup>1</sup> <i>J</i> <sub>P-C</sub> 90.2
12	7.78–7.61	m		130.46	d	<sup>2</sup> <i>J</i> <sub>P-C</sub> 12.5
				130.25	d	<sup>2</sup> <i>J</i> <sub>P-C</sub> 12.5
13	7.78–7.61	m		133.67	d	<sup>3</sup> <i>J</i> <sub>P-C</sub> 9.7
				133.46	d	<sup>3</sup> <i>J</i> <sub>P-C</sub> 9.7
14	7.78–7.61	m		134.97	d	<sup>4</sup> <i>J</i> <sub>P-C</sub> 2.8
				134.93	d	<sup>4</sup> <i>J</i> <sub>P-C</sub> 2.8
CO				241.16	s	

<sup>a</sup> See Fig. 2 for atom numbering scheme.

\* The peaks for protons 6 and 7 overlap and the multiplicity is described as inferred from the observed patterns and that expected for these peaks.

two P–Me doublets at  $\delta$  3.18 and 2.85, the ratio of intensities of the two isomers varying from experiment to experiment. Similarly the <sup>31</sup>P NMR spectrum exhibits two resonances at  $\delta$  26.04 and 13.52 with a similar ratio of intensities. The phosphonium salt was sufficiently pure (NMR) that it could be used as obtained for the synthesis of **1**.

The phosphonium 1-indenylyde **1** was obtained in excellent yield (87%) by deprotonation of the corresponding phosphonium iodide with an excess of NaH in THF. Although this reaction is slow,

**Scheme 1.** The synthesis of **1**.

the product is easily separated and purified. Analytically pure material and X-ray quality crystals of **1** were obtained by recrystallization from a CH<sub>2</sub>Cl<sub>2</sub> solution layered with hexanes and kept at –30 °C.

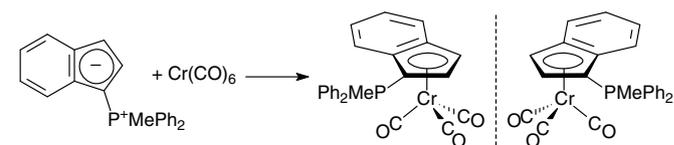
Using the indenyl system offers several advantages relative to the analogous Cp-derived phosphonium ylide, C<sub>5</sub>H<sub>4</sub>PMePh<sub>2</sub>. Thus, for instance, the precursor phosphine, 1-C<sub>9</sub>H<sub>7</sub>PPh<sub>2</sub>, is thermally more stable than is CpPPh<sub>2</sub> which decomposes if not used immediately after synthesis [8,9]. In addition, during the deprotonation of the two phosphonium salts, the resulting methyldiphenylphosphonium 1-indenylyde, **1**, is formed in higher yields than is C<sub>5</sub>H<sub>4</sub>PMePh<sub>2</sub> [1,8]. Finally, **1** also exhibits higher solubilities in aromatic solvents than does C<sub>5</sub>H<sub>4</sub>PMePh<sub>2</sub> [1,8].

To synthesize **2**, **1** was refluxed in diglyme with an excess (2–3 equiv.) of Cr(CO)<sub>6</sub> (Scheme 2), and gave **2** in 40% yield. Purification to yield analytically pure material and X-ray quality crystals was accomplished by recrystallization from a CH<sub>2</sub>Cl<sub>2</sub> solution layered with hexanes and kept at –30 °C.

### 3.2. IR and NMR Spectra of **1** and **2**

The IR spectrum of **2** in CH<sub>2</sub>Cl<sub>2</sub> exhibits  $\nu$ (CO) at 1916 (s), 1816 (s) and 1802 (sh) cm<sup>-1</sup> (Fig. 1). Both the frequencies and the relative intensities of the carbonyl bands are similar to those of the related phosphonium cyclopentadienylyde complexes Cr( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>PMePh<sub>2</sub>)(CO)<sub>3</sub> [1] and Cr( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>PPh<sub>3</sub>)(CO)<sub>3</sub> [10], although the doubly degenerate *E* mode is clearly broadened because of the asymmetry in the structure and loss of threefold symmetry in the compound.

Fig. 2 shows the scheme used to label the various <sup>1</sup>H and <sup>13</sup>C sites in **1** and **2**. <sup>1</sup>H NMR spectra of **1** and **2** are shown in Figs. 3 and 4, respectively, and <sup>1</sup>H and <sup>13</sup>C NMR assignments for **1** and **2** are given in Tables 1 and 2, respectively. Although there is in some cases overlapping of resonances, NOESY, COSY, HSQC and HMBC spectra were acquired for both compounds and made possible <sup>1</sup>H and <sup>13</sup>C assignments which are unambiguous.

**Scheme 2.** The synthesis of the chromium complex **2**, demonstrating the nature of the planar chirality which is created on coordination.

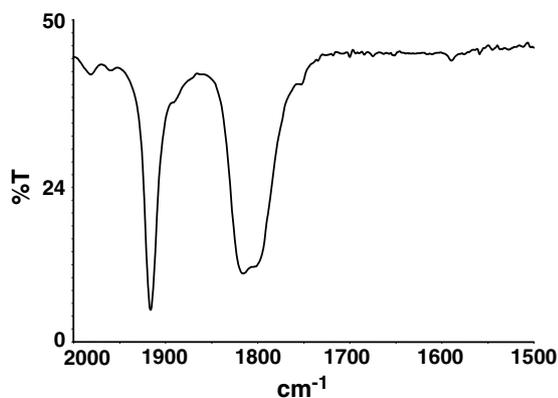


Fig. 1. The IR spectrum of  $\text{Cr}(\eta^5\text{-1-C}_9\text{H}_6\text{PMePh}_2)(\text{CO})_3$  (**2**) in  $\text{CH}_2\text{Cl}_2$ .

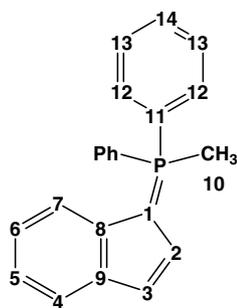


Fig. 2. The labeling scheme used for the NMR assignments of **1** and **2**.

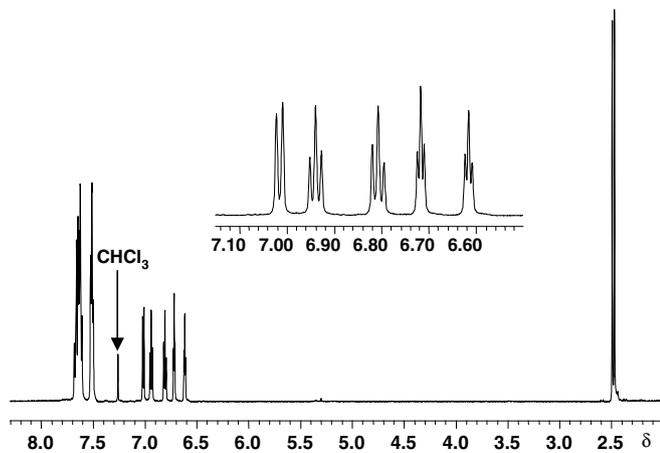


Fig. 3. The  $^1\text{H}$  NMR spectrum of  $1\text{-C}_9\text{H}_6\text{PMePh}_2$  (**1**) in  $\text{CDCl}_3$ .

The indenyl  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts and coupling constants of **1** are very similar to those of the related phosphonium 1-indenylidene  $1\text{-C}_9\text{H}_6\text{P}(\text{CH}_2\text{Ph})\text{Ph}_2$  and  $1\text{-C}_9\text{H}_6\text{P}(\text{CH}_2\text{C}_6\text{F}_5)\text{Ph}_2$  [5]. The  $^{13}\text{C}$  chemical shift of the C(1) resonance of **1** ( $\delta$  66.1) is at a slightly lower field than those of  $1\text{-C}_9\text{H}_6\text{P}(\text{CH}_2\text{Ph})\text{Ph}_2$  ( $\delta$  59.9) and  $1\text{-C}_9\text{H}_6\text{P}(\text{CH}_2\text{C}_6\text{F}_5)\text{Ph}_2$  ( $\delta$  62.2) [5], but 13 ppm to higher field than the ylidic carbon resonance of  $\text{C}_5\text{H}_4\text{PMePh}_2$  ( $\delta$  79.2) [1]. Interestingly, the chemical shift of the C(1) resonance of **1** is  $\sim 17.5$  ppm to higher field than that of the corresponding resonance of 1-diphenylphosphinoind-2-ene ( $\delta$  48.6) [6a] while  $^1J_{\text{P-C}}$  in **1** (120.8 Hz) is significantly higher than that of 1-diphenylphosphinoind-2-ene (33.5 Hz) [6a]. This increase in  $^1J_{\text{P-C}}$  is to be anticipated [6b]. The  $^{31}\text{P}$  NMR chemical shift of **1** ( $\delta$  5.69) is at a slight higher field than that of the related  $\text{C}_5\text{H}_4\text{PMePh}_2$  ( $\delta$  7.95) [1].

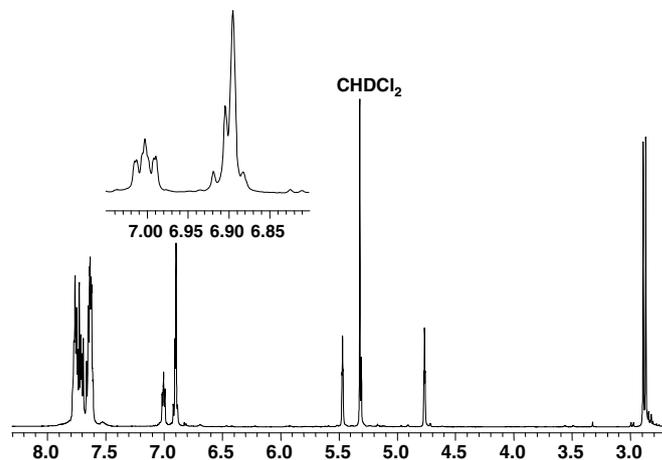


Fig. 4. The  $^1\text{H}$  NMR spectrum of  $\text{Cr}(\eta^5\text{-1-C}_9\text{H}_6\text{PMePh}_2)(\text{CO})_3$  (**2**) in  $\text{CD}_2\text{Cl}_2$ .

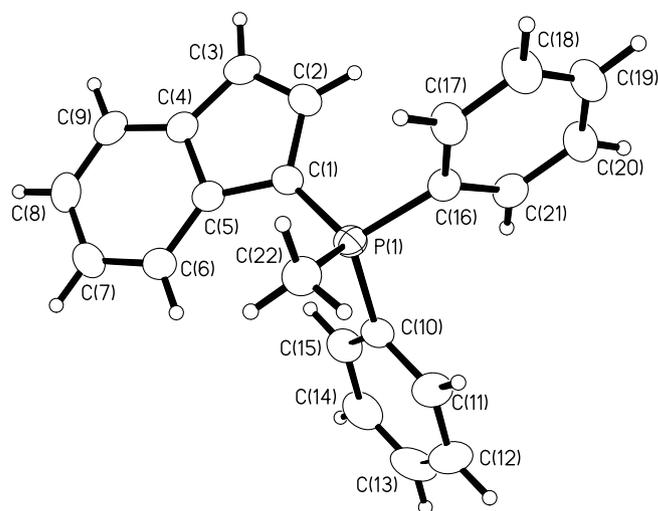


Fig. 5. The molecular structure of  $1\text{-C}_9\text{H}_6\text{PMePh}_2$ .

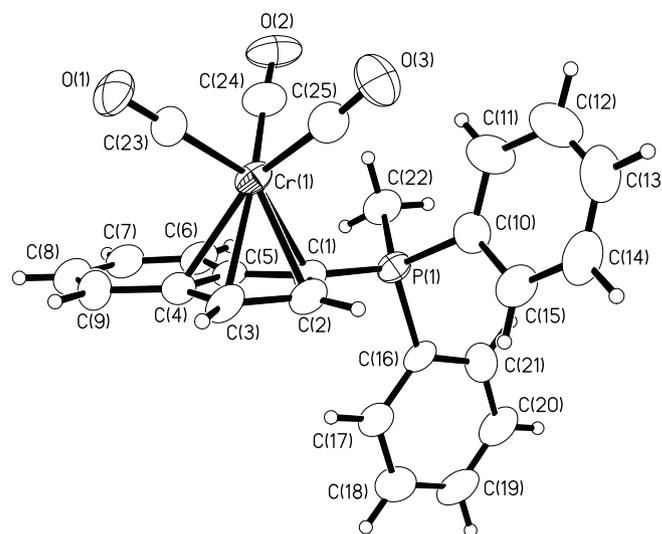


Fig. 6. The molecular structure of  $\text{Cr}(\eta^5\text{-1-C}_9\text{H}_6\text{PMePh}_2)(\text{CO})_3$ .

Coordination of **1** to the  $\text{Cr}(\text{CO})_3$  moiety results in significant changes in the  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR parameters of the ligand. In the  $^1\text{H}$  NMR spectrum of **2**, the  $\text{C}_5\text{H}_4$  protons H(2) and H(3) shift

**Table 3**  
Structural data for compounds **1** and **2**

	<b>1</b>	<b>2</b>
Empirical formula, fw	C <sub>22</sub> H <sub>19</sub> P, 314.34	C <sub>25.50</sub> H <sub>20</sub> ClCrO <sub>3</sub> P, 492.84
Temperature (K)	180(2)	180(2)
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Orthorhombic
Space group	<i>P2</i> (1)/ <i>c</i>	<i>Pna</i> 2(1)
<i>a</i> (Å)	9.9353(18)	15.7408(18)
<i>b</i> (Å)	17.900(3)	18.114(2)
<i>c</i> (Å)	10.0935(18)	8.5337(10)
$\alpha$ (°)	90	90
$\beta$ (°)	112.681(4)	90
$\gamma$ (°)	90	90
<i>V</i> (Å <sup>3</sup> )	2323.09(18)	2433.2(5)
<i>Z</i>	4	4
$\rho$ (calculated) (Mg/m <sup>3</sup> )	1.261	1.345
Absorption coefficient (mm <sup>-1</sup> )	0.163	0.669
<i>F</i> (000)	664	1012
Crystal size (mm <sup>3</sup> )	0.40 × 0.06 × 0.04	0.35 × 0.15 × 0.04
Theta range for data collection	2.22–25.00°	2.25–21.75°
Index ranges	–11 ≤ <i>h</i> ≤ 11, –21 ≤ <i>k</i> ≤ 20, –11 ≤ <i>l</i> ≤ 11	–16 ≤ <i>h</i> ≤ 16, –18 ≤ <i>k</i> ≤ 18, –8 ≤ <i>l</i> ≤ 8
Reflections collected	9436	15 526
Independent reflections	2906 [R(int) = 0.0697]	2863 [R(int) = 0.0601]
Completeness to theta = 25.00°	100.0%	99.7%
Absorption correction	Empirical	Multi-scan
Maximum and minimum transmission	0.4463 and 0.3000	0.9737 and 0.7995
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	2906/0/208	2863/1/271
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.00	1.000
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0455, <i>wR</i> <sub>2</sub> = 0.0873	<i>R</i> <sub>1</sub> = 0.0421, <i>wR</i> <sub>2</sub> = 0.0981
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0723, <i>wR</i> <sub>2</sub> = 0.0919	<i>R</i> <sub>1</sub> = 0.0528, <i>wR</i> <sub>2</sub> = 0.1037
Largest difference in peak and hole	0.393 and –0.332 e Å <sup>-3</sup>	0.295 and –0.227 e Å <sup>-3</sup>

**Table 4**  
Selected bond lengths and angles for **1** and **2**

Bond (Å)	<b>1</b>	C <sub>5</sub> H <sub>4</sub> PMePh <sub>2</sub>		<b>2</b>	Cr(η <sup>5</sup> -C <sub>5</sub> H <sub>4</sub> PMePh <sub>2</sub> )(CO) <sub>3</sub>
		(Molecule 1)	(Molecule 2)		
P(1)–C(1)	1.711(2)	1.7277(17)	1.7268(17)	1.753(5)	1.759(3)
P–Me	1.787(2)	1.799(2)	1.7921(19)	1.781(5)	1.789(3)
P–Ph avg.	1.788	1.81	1.802	1.788	1.796
M–C <sub>5</sub> Centroid				1.854	1.848
C(1)–C(2)	1.420(3)	1.429(3)	1.413(2)	1.443(7)	1.427(4)
C(1)–C(5)	1.432(3)	1.414(3)	1.429(2)	1.461(7)	1.429(4)
C(2)–C(3)	1.364(3)	1.374(3)	1.384(2)	1.387(7)	1.392(4)
C(4)–C(5)	1.423(3)	1.384(3)	1.383(3)	1.405(7)	1.397(4)
C(3)–C(4)	1.421(3)	1.405(3)	1.407(3)	1.427(7)	1.422(4)
C(1)–metal				2.170(5)	2.185(2)
C(2)–metal				2.163(5)	2.204(2)
C(3)–metal				2.201(5)	2.226(3)
C(4)–metal				2.259(5)	2.217(3)
C(5)–metal				2.278(5)	2.191(3)
<b>Bond angles (°)</b>					
C(1)–P–Me	111.90(10)	111.46(9)	111.96(9)	112.6(2)	111.08(13)
C(1)–P–Ph avg.	111.16	111.44	110.64	109.6	109.78
Me–P–Ph avg.	107.05	106.96	108.44	108.6	109.38
Ph–P–Ph	108.33(10)	108.37(8)	106.55(7)	107.8(2)	107.37(12)
P–C(1)–C <sub>5</sub> Centroid	174.9	172.4	178.1	174.7	178.9
C(1)–C(2)–C(3)	110.1(2)	107.42(19)	108.36(16)	109.3(5)	108.3(3)
C(2)–C(3)–C(4)	108.2(2)	108.85(18)	108.16(18)	107.9(5)	108.3(3)
C(3)–C(4)–C(5)	107.96(19)	108.74(18)	108.87(15)	109.6(5)	108.3(3)
C(4)–C(5)–C(1)	107.09(18)	107.47(18)	107.50(17)	106.8(4)	108.0(3)
C(5)–C(1)–C(2)	106.64(19)	107.51(16)	107.11(16)	106.4(4)	107.1(2)

Data for C<sub>5</sub>H<sub>4</sub>PMePh<sub>2</sub> and Cr(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>PMePh<sub>2</sub>)(CO)<sub>3</sub> are from Ref. [1].

upfield from  $\delta$  6.74 and 6.64 in the uncomplexed ligand to  $\delta$  4.76 and 5.47. A similar upfield shift for the ring protons was observed upon complexation of the related ylide, C<sub>5</sub>H<sub>4</sub>PMePh<sub>2</sub>, but the changes were somewhat smaller (~1.5 ppm vs. ~2 ppm) [1]. The P–Me resonance of **1** (H10) shift downfield from  $\delta$  2.48 to  $\delta$  2.88, but there is little change in the phenyl region of the spectrum.

The <sup>13</sup>C NMR of **2** reveals some interesting changes. The resonance of the ylidic carbon, C(1), shifts from  $\delta$  66.14 in **1** to  $\delta$  57.2 in **2**, a change similar to that observed for the ylidic carbon of C<sub>5</sub>H<sub>4</sub>PMePh<sub>2</sub> on complexation albeit smaller in magnitude [1]. The resonances of the C<sub>5</sub> ring carbons C(2) and C(3) also shift, from  $\delta$  126.30 and 105.00 to  $\delta$  95.68 and 80.31, respectively. The resonances of the two other C<sub>5</sub> ring carbons C(8) and C(9) also shift dramatically on complexation, from  $\delta$  137.79 and 135.42 to  $\delta$  109.80 and 109.72. This shift in the resonances of carbons C(8) and C(9) resembles the shift seen in the other C<sub>5</sub> carbon resonances (carbons C(2) and C(3)). The two resonances of carbons C(8) and C(9) overlap so closely that they could not be distinguished conclusively in spite of the various 2D NMR techniques employed.

Another feature of interest in the <sup>13</sup>C NMR spectrum of **2** is the inequivalence of the diastereotopic P–Ph groups. This leads to two distinct sets of peaks for these carbons with identical coupling constants (see Table 2). The CO resonance of **2** appears at  $\delta$  241.14, while the <sup>31</sup>P NMR resonance of **2** is observed at lower field ( $\delta$  19.84) than that of **1** ( $\delta$  5.69). Similar shifts occur on coordination of C<sub>5</sub>H<sub>4</sub>PMePh<sub>2</sub> to chromium in Cr(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>PMePh<sub>2</sub>)(CO)<sub>3</sub>.

### 3.3. Molecular structures of **1** and **2**

The molecular structures of **1** and **2** are shown in Figs. 5 and 6, respectively. The structural data for **1** and **2** are listed in Table 3, selected bond lengths and angles in Table 4. Also included in Table 4 for purposes of comparison are the bond lengths and angles for methylidiphenylphosphonium cyclopentadienylyde, and of its chromium(0) complex [1].

As can be seen, the bond lengths and angles are largely as would be anticipated. The P(1)–C(1) bond length is of interest because, as

in the case of phosphonium cyclopentadienylides in general, it provides a useful estimation of the P–C double bond character and hence the relative contributions of the resonance structures **1a** and **1b** to the bonding [1,2g]. Thus the P(1)–C(1) bond of **1**, at 1.711(2) Å, is significantly shorter than the P–Ph bonds in this molecule (average 1.788 Å, typical of P–C single bond in phenyl phosphonium ylides), and is shorter also than the P–C bonds of both the analogous Cp derived ylide, C<sub>5</sub>H<sub>4</sub>PMePh<sub>2</sub> (1.727 Å average) [1] and the Ramirez ylide C<sub>5</sub>H<sub>4</sub>PPh<sub>3</sub> (1.718 (2) Å) [2g]. It is also shorter than the P(1)–C(1) bond length of the phosphonium 1-indenylide, 1-C<sub>9</sub>H<sub>6</sub>P(CH<sub>2</sub>Ph)Ph<sub>2</sub>, which is 1.733(4) Å [5]. The shortening of the P(1)–C(1) indicates that the P(1)–C(1) bond in **1** exhibits greater double bond character than in the other ylides. All, of course, are much longer than the P=CH<sub>2</sub> bond in Ph<sub>3</sub>P=CH<sub>2</sub> (1.66 Å) [11], a typical example of a non-resonance stabilized ylide with considerable double bond character.

The C<sub>5</sub> ring bonds of **1** are on average longer than the C<sub>5</sub> ring bonds of the Ramirez ylide and C<sub>5</sub>H<sub>4</sub>PMePh<sub>2</sub> [1,2g]. The C–C–C bond angles of the C<sub>5</sub> ring in **1** are all close to the values expected for a regular pentagon (108°), and the similarity in the C–C lengths tend to provide evidence of delocalization of the π bond electron density.

On coordination to the –Cr(CO)<sub>3</sub> fragment, the ylidic ligand undergoes several modifications. Elongation of the P(1)–C(1) bond is observed, which is typical of this class of ligand upon coordination [1]. The P(1)–C(1) bond length of 1.753(5) Å in **2** is similar in length to those observed in the complexes Cr(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>PMePh<sub>2</sub>)(CO)<sub>3</sub> (1.759(3) Å) and Cr(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>PPh<sub>3</sub>)(CO)<sub>3</sub> (1.751(5) Å and 1.755(6) Å). The increase in bond length is indicative of a greater contribution of the zwitterionic resonance structure of the ligand upon coordination indicating a greater degree of aromatic character. The P(1)–C(1)–C<sub>5</sub>(centroid) bond angle (174.7°) remains similar to that observed in the free ligand, but falls between those observed for Cr(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>PMePh<sub>2</sub>)(CO)<sub>3</sub> (178.9°) and Cr(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>PPh<sub>3</sub>)(CO)<sub>3</sub> (173.4° and 169.0°) [1,2g]. The bond lengths of the C<sub>5</sub> ring of **2** are, on average, longer than in the free ligand, as observed for Cr(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>PMePh<sub>2</sub>)(CO)<sub>3</sub> [1].

An interesting consequence of using the prochiral phosphonium 1-indenylide is that, on coordination, a pair of enantiomers, exhibiting planar chirality, are formed (Scheme 2). This property is anticipated to be of importance if catalytically active complexes of **1** are formed in future.

#### 4. Summary

The new aromatic ligand methyldiphenylphosphonium 1-indenylide (1-C<sub>9</sub>H<sub>6</sub>PMePh<sub>2</sub>, **1**) and its chromium(0) complex, Cr(η<sup>5</sup>-1-C<sub>9</sub>H<sub>6</sub>PMePh<sub>2</sub>)(CO)<sub>3</sub> (**2**) have been synthesized and characterized. The molecular structures of both compounds have been obtained, and compound **2** is shown to exhibit planar chirality resulting from coordination of the prochiral aromatic ligand.

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#### Appendix A. Supplementary material

CCDC 688424 and 688425 contain the supplementary crystallographic data for 1-C<sub>9</sub>H<sub>6</sub>PMePh<sub>2</sub> and Cr(η<sup>5</sup>-1-C<sub>9</sub>H<sub>6</sub>PMePh<sub>2</sub>)(CO)<sub>3</sub>. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Crystallographic details, including figures of 1-C<sub>9</sub>H<sub>6</sub>PMePh<sub>2</sub> (**1**) and Cr(η<sup>5</sup>-1-C<sub>9</sub>H<sub>6</sub>PMePh<sub>2</sub>)(CO)<sub>3</sub> (**2**), showing complete numbering schemes and thermal ellipsoid figures, and tables of positional and thermal parameters and bond lengths and angles. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2008.05.027](https://doi.org/10.1016/j.jorganchem.2008.05.027).

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