Organometallics 1994, *13*, 2677–2681

Metal-Assisted Cleavage of a C–O Bond of a P-Bound Bifunctional Phosphine Ligand

Paul Steinert and Helmut Werner*

Institut für Anorganische Chemie der Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

Received December 6, 1993[•]

Treatment of $[IrCl(C_2H_4)_2]_2$ (**1**) with the phosphino ester $iPr_2PCH_2CO_2Me$ affords the mononuclear complex *trans*-$[IrCl(C_2H_4)(iPr_2PCH_2CO_2Me\text{-}\kappa P)_2]$ (**2**), which reacts with CO to give *trans*-$[IrCl(CO)(iPr_2PCH_2CO_2Me\text{-}\kappa P)_2]$ (**3**) and with HC≡CR to give $[IrH(C{\equiv}CR)Cl(iPr_2PCH_2CO_2Me\text{-}\kappa P)(iPr_2PCH_2CO_2Me\text{-}\kappa^2 P,O)]$ (R = Ph (**4**), CO_2Me (**5**)). Upon heating, the alkynylhydridoiridium compounds **4** and **5** rearrange to yield the isomeric vinylidenemetal derivatives *trans*-$[IrCl({=}C{=}CHR)(iPr_2PCH_2CO_2Me\text{-}\kappa P)_2]$ (R = Ph (**6**), CO_2Me (**7**)). Reaction of **3**, **6**, and **7** with Al_2O_3/H_2O leads to cleavage of a CH_3–O bond of one phosphino ester ligand and gives the chelate complexes $[Ir(L)(iPr_2PCH_2CO_2Me\text{-}\kappa P)(iPr_2PCH_2CO_2\text{-}\kappa^2 P,O)]$ (L = CO (**8**), C=CHPh (**9**), $C{=}CHCO_2Me$ (**10**)) in 80–90% yield. Compound **8** reacts with methyl iodide by oxidative addition to form the octahedral complex $[IrI(CH_3)(CO)(iPr_2PCH_2CO_2Me\text{-}\kappa P)(iPr_2PCH_2CO_2\text{-}\kappa^2 P,O)]$ (**11**). The X-ray crystal structure of **8** has been determined (triclinic, space group $P\bar{1}$ (No. 2), with a = 9.124(5) Å, b = 11.301(7) Å, c = 12.126(6) Å, α = 79.34(4)°, β = 78.92(4)°, γ = 71.56(5)°, and Z = 2).

Introduction

We have recently shown that the use of the bifunctional phosphines $iPr_2P(CH_2)_2OMe$, $iPr_2P(CH_2)_nNMe_2$, and $iPr_2PCH_2CO_2R$, which behave as "hemilabile" chelating ligands,[1] not only support the C—H activation of simple olefins such as ethene[2] but can also promote the rearrangement of terminal alkynes to vinylidene[3] and even allenylidene units.[4,5] When we attempted, in a continuation of our work on rhodium compounds of the general type $[RhCl(\kappa\text{-P–O})(\kappa^2\text{-P–O})]$,[5,6] to prepare the corresponding iridium derivatives, we observed that instead of the expected square-planar complex $[IrCl(iPr_2PCH_2CH_2OMe\text{-}\kappa P)(iPr_2PCH_2CH_2OMe\text{-}\kappa^2 P,O)]$ the octahedral C—H activation product $[IrHCl(CH_2OCH_2CH_2PiPr_2\text{-}\kappa^2 P,C)(iPr_2PCH_2CH_2OMe\text{-}\kappa^2 P,O)]$ was formed.[7] In the present paper we describe that with the phosphino ester $iPr_2PCH_2CO_2Me$ iridium(I) and iridium(III) compounds, including the vinylidene derivatives *trans*-$[IrCl({=}C{=}CHR)(iPr_2PCH_2CO_2R\text{-}\kappa P)_2]$, are obtained. In particular, under mild conditions (with Al_2O_3/H_2O as a support) a metal-assisted conversion of a *P*-coordinated $iPr_2PCH_2CO_2Me$ to a chelating $iPr_2PCH_2CO_2^-$ ligand by cleavage of a CH_3–O bond takes place.

Results and Discussion

Preparation of (Ethene)-, Carbonyl-, and Vinylideneiridium(I) Complexes and of Alkynylhydridoiridium(III) Complexes with $iPr_2PCH_2CO_2Me$ as Ligand.

The chloro-bridged ethene complex $[IrCl(C_2H_4)_2]_2$ (**1**) reacts with $iPr_2PCH_2CO_2Me$ in a pentane suspension at room temperature by partial displacement of the olefinic ligands to give the mononuclear compound *trans*-$[IrCl(C_2H_4)(iPr_2PCH_2CO_2Me\text{-}\kappa P)_2]$ (**2**) in almost quantitative yield. The ^1H and ^{31}P NMR spectra of **2**, which has been isolated as an orange, only slightly air-sensitive solid, reveal that the two phosphino ester ligands are equivalent and in positions *trans* to each other (see Scheme 1). Furthermore, the appearance of one band in the IR spectrum at 1732 cm^{-1} for the C=O stretching frequency indicates[8] that the ester groups of the phosphines are not involved in the coordination to the metal.

When CO is passed through a solution of **2** in benzene, a rapid displacement of ethene by carbon monoxide occurs and the carbonyl complex *trans*-$[IrCl(CO)(iPr_2PCH_2CO_2Me\text{-}\kappa P)_2]$ (**3**) is formed again in excellent yield. Whereas in the IR spectrum of **3** the ν(C≡O) band is observed at 1940 cm^{-1}, the C=O stretch appears at nearly the same position (1728 cm^{-1}) as in the spectrum of **2**. In addition, treatment of **2** in benzene with HC≡CPh and $HC{\equiv}CCO_2Me$ spontaneously leads to the substitution of the ethene ligand and to the formation of the alkynylhydridoiridium(III) compounds $[IrH(C{\equiv}CR)Cl(iPr_2PCH_2CO_2Me\text{-}\kappa P)(iPr_2PCH_2CO_2Me\text{-}\kappa^2 P,O)]$ (R = Ph (**4**), CO_2Me (**5**)). If the reaction of **2** with $HC{\equiv}CCO_2Me$ in C_6D_6 is monitored by NMR spectroscopy, the temporary appearance of a singlet at δ 2.10, assigned to the *H*C≡C proton, indicates that the coordination of the alkyne to the metal probably occurs initially (for comparison see refs 7a and 9). The subsequent intramolecular oxidative addition is accompanied by the chelation of one phosphino ester ligand, probably via the C=O oxygen of the ester unit. The IR spectra of **4** and **5** show two absorptions at about 1730 and 1650 cm^{-1}, which are assigned to the C=O

[•] Abstract published in *Advance ACS Abstracts*, May 15, 1994.

(1) (a) Jeffrey, J. C.; Rauchfuss, T. B. *Inorg. Chem.* **1979**, *18*, 2658–2666. (b) Review: Bader, A.; Lindner, E. *Coord. Chem. Rev.* **1991**, *108*, 27–110.

(2) Schulz, M.; Werner, H. *Organometallics* **1992**, *11*, 2790–2795.

(3) Werner, H.; Stark, A.; Schulz, M.; Wolf, J. *Organometallics* **1992**, *11*, 1126–1130.

(4) Stark, A. Dissertation, Universität Würzburg, to be submitted.

(5) Windmüller, B. Diploma Thesis, Universität Würzburg, 1992.

(6) (a) Werner, H.; Hampp, A.; Peters, K.; Peters, E. M.; Walz, L.; von Schnering, H. G. *Z. Naturforsch.* **1990**, *45B*, 1548–1558. (b) Werner, H.; Hampp, A.; Windmüller, B. *J. Organomet. Chem.* **1992**, *435*, 169–183.

(7) (a) Schulz, M. Dissertation, Universität Würzburg, 1991. (b) Schulz, M.; Werner, H. *J. Am. Chem. Soc.*, to be submitted for publication.

(8) Hesse, M.; Meier, H.; Zeeh, B. *Spektroskopische Methoden in der organischen Chemie*, 4th ed.; Georg Thieme Verlag: Stuttgart, Germany, 1991; p 47.

(9) Höhn, A.; Werner, H. *J. Organomet. Chem.* **1990**, *382*, 255–272.

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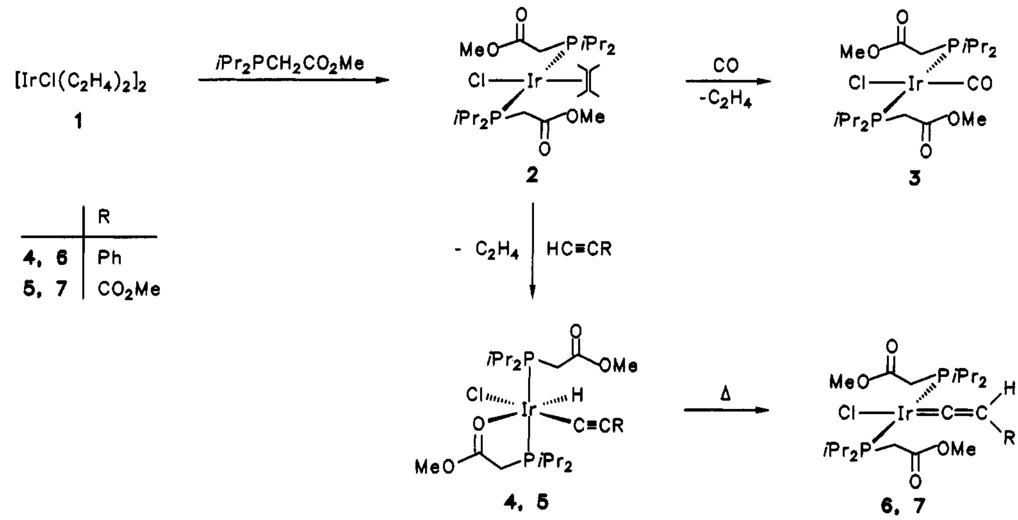
Scheme 1



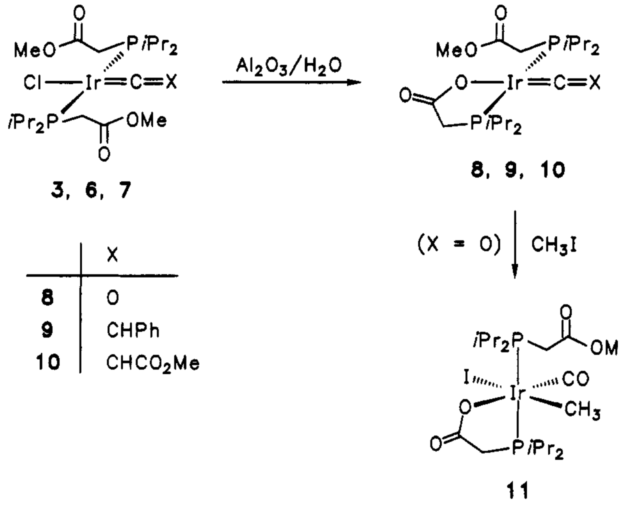
	R
4, 6	Ph
5, 7	CO_2Me

stretching frequencies of the free and the coordinated CO_2R groups. At room temperature, both compounds **4** and **5** are fluxional in solution, as can be seen by the appearance of one broad singlet (doublet in off-resonance) in the ^{31}P NMR spectra. The bond-breaking and bond-forming process is frozen out at low temperature, and thus in the spectrum of **5** at −80 °C the typical AB pattern (with two doublets at δ 18.68 and 34.33) is observed. From the coalescence temperature (−35 °C) and the difference in the chemical shifts of the two resonances a $\Delta G^{\ddagger}$ value of approximately 43 kJ/mol for the dynamic process can be calculated. The large P–P coupling constant of 355 Hz leaves no doubt that in the rigid octahedral molecule of **5** the two phosphorus atoms are in a *trans* disposition.

Warming benzene solutions of the alkynyl hydrido complexes to 80 °C for 15 h (**4**) or 60 h (**5**) gives the isomeric square-planar vinylideneiridium(I) compounds **6** and **7** in moderate to good yields. Both **6** and **7** are deep red, only slightly air-sensitive oils which readily dissolve in all common organic solvents. Similar to the ethene and the carbonyl complexes **2** and **3**, the IR spectra of **6** and **7** each reveal only one ν(C=O) band at about 1730 cm^{-1} and, therefore, the formation of a five-coordinated compound can be excluded. The most typical feature of the ^1H NMR spectra of **6** and **7** is the high-field signal of the $=CHR$ vinylidene proton at δ −2.46 and −2.05, which is reminiscent of the values found for the bis(triisopropylphosphine)-iridium derivatives *trans*-$[IrCl(=C=CHR)(PiPr_3)_2]$.[9,10]

Conversion of a Phosphino Ester to a Phosphinoacetate Ligand. During our attempts to purify the carbonyl and vinylidene complexes **3**, **6**, and **7** by chromatographic techniques using deactivated basic Al_2O_3, we observed that a subsequent reaction occurs which by formal elimination of CH_3Cl gives the novel chelate compounds $[Ir(L)(iPr_2PCH_2CO_2Me\text{-}\kappa P)(iPr_2PCH_2CO_2\text{-}\kappa^2 P,O)]$ (L = CO (**8**), C=CHPh (**9**), C=CHCO$_2$Me (**10**)) in 80–90% yield. Since the starting materials **3**, **6**, and **7** are inert toward water, we assume that the basic aluminum oxide initiates the cleavage of the CH_3—O ester bond and that this process is followed by an intramolecular displacement of the chloride ligand by the phosphinoacetate unit. The carbonyl complex **8** forms bright yellow air-stable crystals, whereas the vinylidene derivatives **9** and **10** are isolated as red or red-violet oils. For all the three compounds correct elemental analyses have been obtained. As far as the spectroscopic data of **8**–**10** are concerned, the common feature is that in the ^1H NMR spectra, in contrast to those of **3**, **6** and **7**, *two* doublets for the PCH_2 protons and *four* signals (doublets of doublets) for the $PCHCH_3$ protons are observed. In agreement with this, the ^{13}C NMR spectra also show *two* resonances for the PCH_2 and *two* signals for the PCH_2CO_2 and PCH_2CO_2Me carbon atoms which not only differ in the chemical shift but, more significantly, in the size of the P—C coupling constant. Accordingly, the ^{31}P NMR spectra of **8**–**10** reveal two resonances as part of an AB system, while in the IR spectra two C=O stretching frequencies attributable to the CO_2^- and the CO_2Me groups are observed.

Scheme 2



	X
8	O
9	CHPh
10	$CHCO_2Me$

The ester cleavage cannot be reversed upon treatment of the chelate complexes with methyl iodide. With a 2-fold excess of CH_3I, compound **8** reacts to give a colorless air-stable oil of the composition $[IrI(CH_3)(CO)(iPr_2PCH_2CO_2Me\text{-}\kappa P)(iPr_2PCH_2CO_2\text{-}\kappa^2 P,O)]$ (**11**), which is an uncharged octahedral iridium(III) complex (see Scheme 2). From the spectroscopic data for **11**, it cannot be unambiguously decided whether the iodo and the methyl ligands are *trans* or *cis* to each other, even though the data would be consistent with a *trans* disposition. The IR as well as the ^1H and ^{31}P NMR spectra leave no doubt that one phosphino ester and one phosphinoacetate ligand are

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(10) Werner, H.; Höhn, A.; Schulz, M. *J. Chem. Soc., Dalton Trans.* **1991**, 777–781.

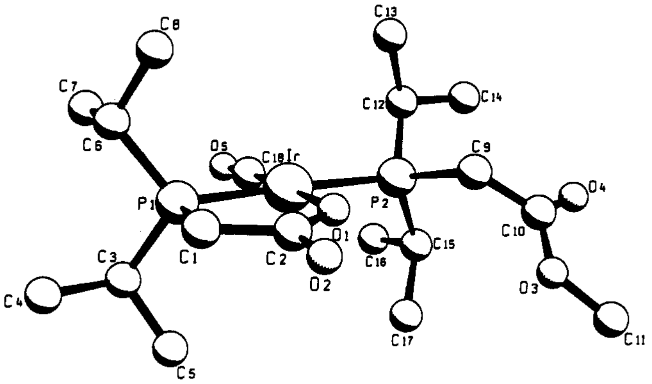

Figure 1. SCHAKAL plot of complex 8.

Table 1. Selected Bond Distances and Angles with Esd's for 8

	Bond Distances (Å)		
Ir–P1	2.281(1)	P2–C15	1.839(5)
Ir–P2	2.328(1)	O1–C2	1.300(5)
Ir–O1	2.060(3)	O2–C2	1.211(6)
Ir–C18	1.807(5)	O3–C10	1.333(6)
P1–C1	1.824(5)	O3–C11	1.445(8)
P1–C3	1.844(5)	O4–C10	1.192(5)
P1–C6	1.842(6)	O5–C18	1.150(6)
P2–C9	1.855(5)	C1–C2	1.518(7)
P2–C12	1.841(4)	C9–C10	1.492(8)
	Bond Angles (deg)		
P1–Ir–P2	174.39(4)	Ir–P2–C9	112.8(1)
P1–Ir–O1	82.76(9)	Ir–P2–C12	112.7(2)
P1–Ir–C18	93.8(2)	Ir–P2–C15	114.4(1)
P2–Ir–O1	91.67(9)	Ir–O1–C2	124.0(3)
P2–Ir–C18	91.7(2)	P1–C1–C2	111.7(3)
O1–Ir–C18	176.4(2)	O1–C2–O2	122.4(5)
Ir–P1–C1	102.4(2)	O1–C2–C1	118.7(4)
Ir–P1–C3	115.4(2)	O2–C2–C1	118.9(4)
Ir–P1–C6	118.5(1)	Ir–C18–O5	177.1(4)

coordinated to the metal, and thus the formation of **11** is understood as an oxidative addition. Even when it is heated, the carbonylmethylmetal complex does not react by an intramolecular ligand-assisted insertion of CO into the $\mathrm{Ir{-}CH_3}$ bond to give an acetyliridium(III) derivative.

Molecular Structure of 8. A single-crystal X-ray diffraction study of the carbonyl complex **8** confirms the structural proposal shown in Scheme 2. The SCHAKAL plot (Figure 1) reveals that the iridium is coordinated in a square-planar fashion with a P1–Ir–O1 bite angle (82.76(9)°) that slightly deviates from the 90° value. The phosphorus–metal–phosphorus axis (angle 174.39(4)°) is almost linear, and the same is true for the O1–Ir–C18–O5 arrangement. Although both phosphorus atoms are linked to three alkyl groups, the two Ir–P bond lengths differ by about 0.05 Å. A similar situation has been found by Podlahová et al. for the tetracoordinated rhodium complex $[\mathrm{Rh(CO)(Ph_2PCH_2CO_2H}\text{-}\kappa P)(\mathrm{Ph_2PCH_2CO_2}\text{-}\kappa^2 P,O)]$, where the two Rh–P distances are 2.346(2) Å (monodentate phosphine) and 2.302(2) Å (chelating phosphine), respectively.[11] In this context we note that square-planar palladium(II) and platinum(II) compounds with phosphino esters $\mathrm{R_2PCH_2CO_2Et}$ (R = *t*Bu, Ph) have been described by both Shaw[12] and Braunstein et al.[13] and that in some of these compounds the ester group cannot only undergo O-metalation (to yield phosphinoacetates) but also activate the adjacent $\mathrm{CH_2}$ unit to give phosphino enolate ligands. With the iridium complexes reported in this work, a similar C-metalation has never been observed.

Experimental Section

All experiments were carried out under an atmosphere of argon using Schlenk-tube techniques. The starting materials **1**[14] and $i\mathrm{Pr_2PCH_2CO_2Me}$[15] were prepared as described in the literature. Melting points were determined by DTA. IR spectra were recorded on a Perkin-Elmer 1420 infrared spectrophotometer and NMR spectra on Varian EM 360 L, JEOL FX 90 Q, and Bruker AMX 400 instruments. Abbreviations used: s = singlet, d = doublet, t = triplet, m = multiplet, vt = virtual triplet; $N = {}^3J(\mathrm{PH}) + {}^5J(\mathrm{PH})$, $N' = {}^2J(\mathrm{PH}) + {}^4J(\mathrm{PH})$ for ^{1}H NMR; $N = {}^1J(\mathrm{PC}) + {}^3J(\mathrm{PC})$, $N' = {}^2J(\mathrm{PC}) + {}^4J(\mathrm{PC})$ for ^{13}C NMR.

Preparation of *trans*-$[\mathrm{IrCl(C_2H_4)}(i\mathrm{Pr_2PCH_2CO_2Me}\text{-}\kappa P)_2]$ (2). A suspension of **1** (101 mg, 0.18 mmol) in 5 mL of pentane was treated with $i\mathrm{Pr_2PCH_2CO_2Me}$ (140 μL, 0.71 mmol) and stirred for 30 min at room temperature. An orange solid precipitated, which was separated from the solution, repeatedly washed with small amounts of pentane, and dried under vacuum: yield 206 mg (91%); mp 78 °C. Anal. Calcd for $\mathrm{C_{20}H_{42}ClIrO_4P_2}$: C, 37.76; H, 6.65. Found: C, 37.77; H, 6.79. IR (KBr): ν(C═O) 1732 cm^{-1}. ^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$): δ 3.22 (s, 6H, $\mathrm{CO_2C}H_3$), 2.85 (m, 4H, $\mathrm{PC}H\mathrm{CH_3}$), 2.43 (vt, N' = 5.6 Hz, 4H, $\mathrm{PC}H_2$), 1.60 (t, J(PH) = 4.5 Hz, 4H, $\mathrm{C_2}H_4$), 1.38 (dvt, N = 15.5, J(HH) = 7.1 Hz, 12H, $\mathrm{PCHC}H_3$), 1.20 (dvt, N = 13.9, J(HH) = 7.0 Hz, 12H, $\mathrm{PCHC}H_3$). ^{31}P NMR (162.0 MHz, $\mathrm{C_6D_6}$): δ 20.16 (s).

Preparation of *trans*-$[\mathrm{IrCl(CO)}(i\mathrm{Pr_2PCH_2CO_2Me}\text{-}\kappa P)_2]$ (3). A slow stream of carbon monoxide was passed through a solution of **2** (56 mg, 0.09 mmol) in 5 mL of benzene for ca. 15 s. A change of color from orange to bright yellow occurred. The solvent was removed under vacuum, and the remaining lemon yellow air-stable solid was repeatedly washed with pentane: yield 50 mg (90%); mp 77 °C. Anal. Calcd for $\mathrm{C_{19}H_{38}ClIrO_5P_2}$: C, 35.87; H, 6.02. Found: C, 35.65; H, 5.93. IR ($\mathrm{C_6H_6}$): ν(CO) 1940, ν(C═O) 1728 cm^{-1}. ^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$): δ 3.32 (vt, N' = 7.6 Hz, 4H, $\mathrm{PC}H_2$), 3.21 (s, 6H, $\mathrm{CO_2C}H_3$), 2.67 (m, 4H, $\mathrm{PC}H\mathrm{CH_3}$), 1.31 (dvt, N = 16.5, J(HH) = 7.1 Hz, 12H, $\mathrm{PCHC}H_3$), 1.19 (dvt, N = 14.7, J(HH) = 7.0 Hz, 12H, $\mathrm{PCHC}H_3$). ^{31}P NMR (162.0 MHz, $\mathrm{C_6D_6}$): δ 35.54 (s).

Preparation of $[\mathrm{IrH(C{\equiv}CPh)Cl}(i\mathrm{Pr_2PCH_2CO_2Me}\text{-}\kappa P)(i\mathrm{Pr_2PCH_2CO_2Me}\text{-}\kappa^2 P,O)]$ (4). A solution of **2** (48 mg, 0.08 mmol) in 5 mL of benzene was treated with phenylacetylene (8 μL, 0.08 mmol) and stirred for 5 min at room temperature. A change of color from orange to red occurred. The solvent was removed under vacuum, and the red-brown residue was repeatedly washed with small amounts of pentane and thoroughly dried: yield 44 mg (83%). Anal. Calcd for $\mathrm{C_{28}H_{44}ClIrO_4P_2}$: C, 43.97; H, 6.24. Found: C, 43.63; H, 6.11. IR ($\mathrm{C_6H_6}$): ν(IrH) 2272, ν(C≡C) 2105, ν(C═O) 1729, 1655 cm^{-1}. ^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$): δ 7.29 (m, 5H, $\mathrm{C_6}H_5$), 3.41 (vt, br, 4H, $\mathrm{PC}H_2$), 3.20 (s, 6H, $\mathrm{CO_2C}H_3$), 3.02 (m, 2H, $\mathrm{PC}H\mathrm{CH_3}$), 2.84 (m, 2H, $\mathrm{PC}H\mathrm{CH_3}$), 1.40 (dvt, N = 15.4, J(HH) = 6.9 Hz, 12H, $\mathrm{PCHC}H_3$), 1.32 (dvt, N = 14.8, J(HH) = 7.3 Hz, 6H, $\mathrm{PCHC}H_3$), 1.20 (dvt, N = 15.0, J(HH) = 7.1 Hz, 6H, $\mathrm{PCHC}H_3$), −30.03 (s, br, 1H, Ir*H*, transitional dynamic regime; at 60 MHz t, J(PH) = 13.5 Hz, high-temperature limit at this spectrometer frequency). ^{31}P NMR (162.0 MHz, $\mathrm{C_6D_6}$): δ 25.65 (s, br; d in off-resonance).

Preparation of $[\mathrm{IrH(C{\equiv}CCO_2Me)Cl}(i\mathrm{Pr_2PCH_2CO_2Me}\text{-}\kappa P)(i\mathrm{Pr_2PCH_2CO_2Me}\text{-}\kappa^2 P,O)]$ (5). The preparation is analogous to that described for **4**, using **2** (48 mg, 0.08 mmol) and $\mathrm{HC{\equiv}CCO_2Me}$ (7 μL, 0.08 mmol) as starting materials. A red, only moderately air-sensitive oil is obtained: yield 44 mg (84%). Anal. Calcd for $\mathrm{C_{22}H_{42}ClIrO_6P_2}$: C, 38.17; H, 6.12. Found: C, 38.24; H, 5.88. IR ($\mathrm{C_6H_6}$): ν(IrH) 2275, ν(C≡C) 2099, ν(C═O) 1731, 1681, 1648

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[11] Jegorov, J.; Kratochvil, B.; Langer, V.; Podlahová, J. *Inorg. Chem.* **1984**, *23*, 4288–4291.

[12] Empsall, H. D.; Hyde, E. M.; Pawson, D.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1977**, 1292–1298.

[13] Braunstein, P.; Matt, D.; Dusausoy, Y.; Fischer, J.; Mitschler, A.; Ricard, L. *J. Am. Chem. Soc.* **1981**, *103*, 5115–5125.

[14] Onderdelinden, A. L.; van der Ent, A. *Inorg. Chim. Acta* **1972**, *6*, 420–426.

[15] Burkart, W. Diploma Thesis, Universität Würzburg, 1990.

$\mathrm{cm^{-1}}$. ^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$): δ 3.43 (s, 3H, $\mathrm{C{\equiv}CCO_2C}H_3$), 3.35 (vt, *N'* = 7.3 Hz, 4H, $\mathrm{PC}H_2$), 3.13 (s, 6H, $\mathrm{CO_2C}H_3$), 2.95 (m, 2H, $\mathrm{PC}HCH_3$), 2.81 (m, 2H, $\mathrm{PC}HCH_3$), 1.36 (dvt, *N* = 15.7, *J*(HH) = 7.8 Hz, 6H, $\mathrm{PCHC}H_3$), 1.32 (dvt, *N* = 16.3, *J*(HH) = 8.0 Hz, 6H, $\mathrm{PCHC}H_3$), 1.28 (dvt, *N* = 15.3, *J*(HH) = 7.5 Hz, 6H, $\mathrm{PCHC}H_3$), 1.13 (dvt, *N* = 14.9, *J*(HH) = 7.5 Hz, 6H, $\mathrm{PCHC}H_3$), −29.02 (s, br, 1H, Ir*H*, transitional dynamic regime; at 60 MHz t, *J*(PH) = 13.0 Hz, high-temperature limit at this spectrometer frequency). ^{31}P NMR (36.2 MHz, toluene-d_8, 25 °C): δ 25.83 (s, br; d in off-resonance); at −80 °C AB system, δ(P) 34.33 and 18.68 (both d, *J*(PP) = 355.3 Hz).

Preparation of *trans*-[IrCl(=C=CHPh)(*i*Pr$_2$PCH$_2$CO$_2$Me-*κP*)$_2$] (6). A solution of 4 (67 mg, 0.09 mmol) in 5 mL of benzene was warmed with stirring to 80 °C for 60 h. After the solution was cooled to room temperature, the solvent was removed and the oily residue dissolved in 2 mL of benzene. The solution was chromatographed on $\mathrm{Al_2O_3}$ (neutral, activity grade V). With benzene, a red fraction was eluted which was brought to dryness under vacuum. A deep red, only slightly air-sensitive oil was obtained; yield 32 mg (48%). Anal. Calcd for $\mathrm{C_{26}H_{44}ClIrO_4P_2}$: C, 43.97; H, 6.24. Found: C, 44.38; H, 6.09. IR ($\mathrm{C_6H_6}$): ν(C=O) 1728, ν(C=C) 1652 $\mathrm{cm^{-1}}$. ^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$): δ 7.16 (m, 5H, $\mathrm{C_6}H_5$), 3.40 (vt, *N'* = 7.2 Hz, 4H, $\mathrm{PC}H_2$), 3.16 (s, 6H, $\mathrm{CO_2C}H_3$), 2.94 (m, 4H, $\mathrm{PC}H\mathrm{CH_3}$), 1.35 (dvt, *N* = 16.3, *J*(HH) = 7.1 Hz, 12H, $\mathrm{PCHC}H_3$), 1.20 (dvt, *N* = 14.3, *J*(HH) = 7.0 Hz, 12H, $\mathrm{PCHC}H_3$), −2.46 (t, *J*(PH) = 2.9 Hz, 1H, C=C*H*). ^{13}C NMR (100.6 MHz, $\mathrm{C_6D_6}$): δ 265.17 (t, *J*(PC) = 13.2 Hz, Ir=*C*), 170.65 (vt, *N'* = 4.1 Hz, $C\mathrm{O_2CH_3}$), 128.74, 128.35, 125.46, 125.03 (all s, $C_6\mathrm{H_5}$), 111.06 (t, *J*(PC) = 3.6 Hz, C=*C*HPh), 51.26 (s, $\mathrm{CO_2}C\mathrm{H_3}$), 24.34 (vt, *N* = 18.3 Hz, $\mathrm{P}C\mathrm{H_2}$), 23.18 (vt, *N* = 27.8 Hz, $\mathrm{P}C\mathrm{HCH_3}$), 19.17, 18.17 (both s, $\mathrm{PCH}C\mathrm{H_3}$). ^{31}P NMR (162.0 MHz, $\mathrm{C_6D_6}$): δ 27.01 (s).

Preparation of *trans*-[IrCl(=C=CHCO$_2$Me)(*i*Pr$_2$PCH$_2$CO$_2$Me-*κP*)$_2$] (7). The preparation is analogous to that described for **6**, using **5** (76 mg, 0.11 mmol) as starting material. The reaction mixture, however, was warmed to 80 °C for 15 h (not for 60 h). A red-violet, almost air-stable oil was obtained; yield 59 mg (77%). Anal. Calcd for $\mathrm{C_{22}H_{42}ClIrO_6P_2}$: C, 38.17; H, 6.12. Found: C, 38.86; H, 6.03. IR ($\mathrm{C_6H_6}$): ν(C=O) 1729, 1695, ν(C=C) 1617 $\mathrm{cm^{-1}}$. ^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$): δ 3.47 (s, 3H, $\mathrm{CHCO_2C}H_3$), 3.40 (vt, *N'* = 8.6 Hz, 4H, $\mathrm{PC}H_2$), 3.22 (s, 6H, $\mathrm{PCH_2CO_2C}H_3$), 2.87 (m, 4H, $\mathrm{PC}H\mathrm{CH_3}$), 1.30 (dvt, *N* = 16.8, *J*(HH) = 7.1 Hz, 12H, $\mathrm{PCHC}H_3$), 1.19 (dvt, *N* = 14.0, *J*(HH) = 7.0 Hz, 12H, $\mathrm{PCHC}H_3$), −2.05 (t, *J*(PH) = 2.3 Hz, 1H, C=C*H*). ^{13}C NMR (100.6 MHz, $\mathrm{C_6D_6}$): δ 256.61 (t, *J*(PC) = 12.4 Hz, Ir=*C*), 170.45 (m, $\mathrm{CH_2}C\mathrm{O_2CH_3}$), 151.54 (s, $\mathrm{CH}C\mathrm{O_2CH_3}$), 103.20 (t, *J*(PC) = 2.5 Hz, $\mathrm{C{=}}C\mathrm{HCO_2CH_3}$), 51.43 (s, $\mathrm{PCH_2CO_2}C\mathrm{H_3}$), 50.42 (s, $\mathrm{CHCO_2}C\mathrm{H_3}$), 24.19 (vt, *N* = 18.9 Hz, $\mathrm{P}C\mathrm{H_2}$), 23.31 (vt, *N* = 29.2 Hz, $\mathrm{P}C\mathrm{HCH_3}$), 18.86, 18.03 (both s, $\mathrm{PCH}C\mathrm{H_3}$). ^{31}P NMR (162.0 MHz, $\mathrm{C_6D_6}$): δ 29.71 (s).

Preparation of [Ir(CO)(*i*Pr$_2$PCH$_2$CO$_2$Me-*κP*)(*i*Pr$_2$PCH$_2$CO$_2$-*κ*^{2}*P*,*O*)] (8). A solution of 3 (86 mg, 0.14 mmol) in 5 mL of benzene was chromatographed on $\mathrm{Al_2O_3}$ (basic, activity grade V). With $\mathrm{CH_2Cl_2}$, a yellow fraction was eluted which was brought to dryness under vacuum. A bright yellow air-stable solid was obtained, which was repeatedly washed with pentane and dried: yield 68 mg (87%). Anal. Calcd for $\mathrm{C_{18}H_{35}IrO_5P_2}$: C, 36.92; H, 6.02. Found: C, 36.69; H, 6.11. IR ($\mathrm{C_6H_6}$): ν(CO) 1945, ν(C=O) 1730, 1670 $\mathrm{cm^{-1}}$. ^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$): δ 3.25 (s, 3H, $\mathrm{CO_2C}H_3$), 3.11 (d, *J*(PH) = 8.5 Hz, 2H, $\mathrm{PC}H_2$), 2.47 (m, 2H, $\mathrm{PC}H\mathrm{CH_3}$), 2.38 (d, *J*(PH) = 8.9 Hz, 2H, $\mathrm{PC}H_2$), 1.73 (m, 2H, $\mathrm{PC}H\mathrm{CH_3}$), 1.25 (dd, *J*(PH) = 16.5, *J*(HH) = 7.1 Hz, 6H, $\mathrm{PCHC}H_3$), 1.13 (dd, *J*(PH) = 14.6, *J*(HH) = 7.0 Hz, 6H, $\mathrm{PCHC}H_3$), 0.99 (dd, *J*(PH) = 16.9, *J*(HH) = 7.0 Hz, 6H, $\mathrm{PCHC}H_3$), 0.84 (dd, *J*(PH) = 14.8, *J*(HH) = 6.9 Hz, 6H, $\mathrm{PCHC}H_3$). ^{13}C NMR (100.6 MHz, $\mathrm{C_6D_6}$): δ 181.42 (dd, *J*(PC) = 14.8 and 8.4 Hz, $\mathrm{PCH_2}C\mathrm{O_2Ir}$), 176.79 (t, *J*(PC) = 9.7 Hz, Ir*C*O), 169.88 (dd, *J*(PC) = 7.8 and 3.3 Hz, $\mathrm{PCH_2}C\mathrm{O_2CH_3}$), 51.41 (s, $\mathrm{PCH_2CO_2}C\mathrm{H_3}$), 25.10 (dd, *J*(PC) = 14.4 and 2.0 Hz, $\mathrm{P}C\mathrm{H_2}$), 24.97 (dd, *J*(PC) = 26.9 and 1.3 Hz, $\mathrm{P}C\mathrm{HCH_3}$), 24.58 (dd, *J*(PC) = 30.6 and 2.0 Hz, $\mathrm{P}C\mathrm{HCH_3}$), 23.91 (d, *J*(PC) = 27.7 Hz, $\mathrm{P}C\mathrm{H_2}$), 18.77 (d, *J*(PC) = 3.8 Hz, $\mathrm{PCH}C\mathrm{H_3}$), 18.54 (d, *J*(PC) = 3.4 Hz, $\mathrm{PCH}C\mathrm{H_3}$), 18.12, 17.92 (both s, $\mathrm{PCH}C\mathrm{H_3}$). ^{31}P NMR (162.0 MHz, $\mathrm{C_6D_6}$): AB system, δ(P) 42.92 and 37.34 (both d, *J*(PP) = 291.1 Hz).

Preparation of [Ir(=C=CHPh)(*i*Pr$_2$PCH$_2$CO$_2$Me-*κP*)(*i*Pr$_2$PCH$_2$CO$_2$-*κ*^{2}*P*,*O*)] (9). The preparation is analogous to that described for 8, using 6 (73 mg, 0.10 mmol) as starting material. A red, only slightly air-sensitive oil was obtained: yield 54 mg (80%). Anal. Calcd for $\mathrm{C_{25}H_{41}IrO_4P_2}$: C, 45.51; H, 6.26. Found: C, 45.79; H, 6.41. IR ($\mathrm{C_6H_6}$): ν(C=O) 1728, 1668, ν(C=C) 1655 $\mathrm{cm^{-1}}$. ^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$): δ 7.00 (m, 5H, $\mathrm{C_6}H_5$), 3.23 (d, *J*(PH) = 7.5 Hz, 2H, $\mathrm{PC}H_2$), 3.22 (s, 3H, $\mathrm{CO_2C}H_3$), 2.69 (m, 2H, $\mathrm{PC}H\mathrm{CH_3}$), 2.48 (d, *J*(PH) = 8.8 Hz, 2H, $\mathrm{PC}H_2$), 1.91 (m, 2H, $\mathrm{PC}H\mathrm{CH_3}$), 1.31 (dd, *J*(PH) = 16.3, *J*(HH) = 6.9 Hz, 6H, $\mathrm{PCHC}H_3$), 1.16 (dd, *J*(PH) = 14.1, *J*(HH) = 7.0 Hz, 6H, $\mathrm{PCHC}H_3$), 1.03 (dd, *J*(PH) = 16.5, *J*(HH) = 6.9 Hz, 6H, $\mathrm{PCHC}H_3$), 0.88 (dd, *J*(PH) = 14.5, *J*(HH) = 7.0 Hz, 6H, $\mathrm{PCHC}H_3$), −1.70 (t, *J*(PH) = 2.8 Hz, 1H, C*H*Ph). ^{13}C NMR (100.6 MHz, $\mathrm{C_6D_6}$): δ 274.68 (t, *J*(PC) = 11.7 Hz, Ir=*C*), 182.93 (dd, *J*(PC) = 13.2 and 7.1 Hz, $\mathrm{PCH_2}C\mathrm{O_2Ir}$), 170.29 (dd, *J*(PC) = 8.1 and 3.1 Hz, $\mathrm{PCH_2}C\mathrm{O_2CH_3}$), 128.33, 124.95, 124.75, 120.67 (all s, $C_6\mathrm{H_5}$), 111.56 (t, *J*(PC) = 4.1 Hz, *C*HPh), 51.35 (s, $\mathrm{CO_2}C\mathrm{H_3}$), 24.51 (dd, *J*(PC) = 14.2 and 2.0 Hz, $\mathrm{P}C\mathrm{H_2}$), 24.34 (d, *J*(PC) = 25.4 Hz, $\mathrm{P}C\mathrm{H_2}$), 23.73 (dd, *J*(PC) = 28.6 and 2.8 Hz, $\mathrm{P}C\mathrm{HCH_3}$), 23.65 (dd, *J*(PC) = 25.4 and 2.0 Hz, $\mathrm{P}C\mathrm{HCH_3}$), 19.10 (d, *J*(PC) = 4.1 Hz, $\mathrm{PCH}C\mathrm{H_3}$), 18.68 (d, *J*(PC) = 4.1 Hz, $\mathrm{PCH}C\mathrm{H_3}$), 18.09, 18.04 (both s, $\mathrm{PCH}C\mathrm{H_3}$). ^{31}P NMR (162.0 MHz, $\mathrm{C_6D_6}$): AB system, δ(P) 31.63 and 26.42 (both d, *J*(PP) = 330.0 Hz).

Preparation of [Ir(=C=CHCO$_2$Me)(*i*Pr$_2$PCH$_2$CO$_2$Me-*κP*)(*i*Pr$_2$PCH$_2$CO$_2$-*κ*^{2}*P*,*O*)] (10). The preparation is analogous to that described for 8, using 7 (94 mg, 0.14 mmol) as starting material. A red-violet, only slightly air-sensitive oil was obtained; yield 72 mg (83%). Anal. Calcd for $\mathrm{C_{21}H_{39}IrO_6P_2}$: C, 39.31; H, 6.13. Found: C, 39.27; H, 6.17. IR ($\mathrm{C_6H_6}$): ν(C=O) 1725, 1690, ν(C=C) 1615 $\mathrm{cm^{-1}}$. ^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$): δ 3.50 (s, 3H, $\mathrm{CHCO_2C}H_3$), 3.24 (s, 3H, $\mathrm{CH_2CO_2C}H_3$), 3.18 (d, *J*(PH) = 8.4 Hz, 2H, $\mathrm{PC}H_2$), 2.65 (m, 2H, $\mathrm{PC}H\mathrm{CH_3}$), 2.43 (d, *J*(PH) = 8.9 Hz, 2H, $\mathrm{PC}H_2$), 1.94 (m, 2H, $\mathrm{PC}H\mathrm{CH_3}$), 1.26 (dd, *J*(PH) = 16.5, *J*(HH) = 7.0 Hz, 6H, $\mathrm{PCHC}H_3$), 1.14 (dd, *J*(PH) = 14.3, *J*(HH) = 7.0 Hz, 6H, $\mathrm{PCHC}H_3$), 1.03 (dd, *J*(PH) = 16.9, *J*(HH) = 7.1 Hz, 6H, $\mathrm{PCHC}H_3$), 0.86 (dd, *J*(PH) = 14.7, *J*(HH) = 6.9 Hz, 6H, $\mathrm{PCHC}H_3$), −1.34 (t, *J*(PH) = 2.4 Hz, 1H, $\mathrm{C}H\mathrm{CO_2CH_3}$). ^{13}C NMR (100.6 MHz, $\mathrm{C_6D_6}$): δ 268.64 (t, *J*(PC) = 11.2 Hz, Ir=*C*), 182.20 (dd, *J*(PC) = 13.3 and 8.1 Hz, $\mathrm{PCH_2}C\mathrm{O_2Ir}$), 170.05 (dd, *J*(PC) = 7.7 and 3.4 Hz, $\mathrm{PCH_2}C\mathrm{O_2CH_3}$), 153.10 (s, $\mathrm{CH}C\mathrm{O_2CH_3}$), 103.72 (t, br, *J*(PC) ≈ 2.0 Hz, $C\mathrm{HCO_2CH_3}$), 51.43 (s, $\mathrm{PCH_2CO_2}C\mathrm{H_3}$), 50.25 (s, $\mathrm{CHCO_2}C\mathrm{H_3}$), 24.28 (dd, *J*(PC) = 15.7 and 1.6 Hz, $\mathrm{P}C\mathrm{H_2}$), 24.01 (d, *J*(PC) = 26.6 Hz, $\mathrm{P}C\mathrm{H_2}$), 23.83 (dd, *J*(PC) = 29.5 and 2.8 Hz, $\mathrm{P}C\mathrm{HCH_3}$), 23.77 (dd, *J*(PC) = 26.0 and 2.0 Hz, $\mathrm{P}C\mathrm{HCH_3}$), 18.81 (d, *J*(PC) = 3.8 Hz, $\mathrm{PCH}C\mathrm{H_3}$), 18.46 (d, *J*(PC) = 3.1 Hz, $\mathrm{PCH}C\mathrm{H_3}$), 17.94 (s, $\mathrm{PCH}C\mathrm{H_3}$). ^{31}P NMR (162.0 MHz, $\mathrm{C_6D_6}$): AB system, δ(P) 35.10 and 30.43 (both d, *J*(PP) = 310.4 Hz).

Preparation of [IrI(CH$_3$)(CO)(*i*Pr$_2$PCH$_2$CO$_2$Me-*κP*)(*i*Pr$_2$PCH$_2$CO$_2$-*κ*^{2}*P*,*O*)] (11). A solution of 8 (71 mg, 0.12 mmol) in 5 mL of benzene was treated with $\mathrm{CH_3I}$ (15 μL, 0.24 mmol) and stirred for 20 h at room temperature. The solvent was removed, the oily residue was dissolved in 3 mL of benzene, and the solution was chromatographed on $\mathrm{Al_2O_3}$ (neutral, activity grade V). With benzene, a light yellow fraction was eluted, which gave after removal of the solvent under vacuum a colorless air-stable oil: yield 66 mg (63%). Anal. Calcd for $\mathrm{C_{19}H_{38}IIrO_5P_2}$: C, 31.37; H, 5.26. Found: C, 31.06; H, 4.99. IR ($\mathrm{C_6H_6}$): ν(CO) 2020, ν (C=O) 1732, 1672 $\mathrm{cm^{-1}}$. ^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$): δ 3.44 (dvt, *N* = 11.1, *J*(HH) = 16.2 Hz, 1H, $\mathrm{PC}H_2$), 3.43 (m, 1H, $\mathrm{PC}H\mathrm{CH_3}$), 3.37 (dvt, *N* = 8.7, *J*(HH) = 14.7 Hz, 1H, $\mathrm{PC}H_2$), 3.24 (s, 3H, $\mathrm{CO_2C}H_3$), 3.17 (dvt, *N* = 8.7, *J*(HH) = 14.7 Hz, 1H, $\mathrm{PC}H_2$), 3.03 (m, 1H, $\mathrm{PC}H\mathrm{CH_3}$), 2.91 (dvt, *N* = 5.2, *J*(HH) = 16.2 Hz, 1H, $\mathrm{PC}H_2$), 2.90 (m, 1H, $\mathrm{PC}H\mathrm{CH_3}$), 2.08 (m, 1H, $\mathrm{PC}H\mathrm{CH_3}$), 1.31 (dvt, *N* = 16.5, *J*(HH) = 7.2 Hz, 3H, $\mathrm{PCHC}H_3$), 1.27 (dvt, *N* = 16.6, *J*(HH) = 7.1 Hz, 3H, $\mathrm{PCHC}H_3$), 1.14 (dvt, *N* = 17.0, *J*(HH) = 7.2 Hz, 6H, $\mathrm{PCHC}H_3$), 1.13 (t, *J*(PH) = 4.8 Hz, 3H, $\mathrm{IrC}H_3$), 1.08 (dvt, *N* = 14.8, *J*(HH) = 7.1 Hz, 3H, $\mathrm{PCHC}H_3$), 0.88 (dvt, *N* = 15.5, *J*(HH) = 8.1 Hz, 3H, $\mathrm{PCHC}H_3$), 0.86 (dvt, *N* = 15.4, *J*(HH) = 6.9 Hz, 3H, $\mathrm{PCHC}H_3$), 0.79 (dvt, *N* = 14.6, *J*(HH) = 7.1 Hz, 3H, $\mathrm{PCHC}H_3$).

^{31}P NMR (81.0 MHz, $CDCl_3$): AB system, δ(P) 3.40 and 2.47 (both d, *J*(PP) = 323.3 Hz).

Crystal Structure Analysis of 8. Single crystals were grown from acetone/pentane. Crystal data (from 23 reflections, 10° < θ < 15°): triclinic, space group $P\bar{1}$, (No. 2); a = 9.124(5) Å, b = 11.301(7) Å, c = 12.126(6) Å, α = 79.34(3)°, β = 78.92(4)°, γ = 71.56(5)°, V = 1153.6 Å^3, Z = 2, d_{calcd} = 1.69 g cm^{-3}, μ(Mo K_α) = 59.2 cm^{-1}; crystal size 0.4 × 0.4 × 0.2 mm; Enraf-Nonius CAD4 diffractometer, Mo Kα radiation (0.709 30 Å), graphite monochromator, zirconium filter (factor 16.4); T = 293 K; $\omega/2\theta$ scan, 2θ(max) = 46°; 3425 reflections measured, 3187 independent reflections, 3073 regarded as being observed ($F_o > 3\sigma(F_o)$). Intensity data were corrected for Lorentz and polarization effects, and an empirical absorption correction (ψ-scan method) was applied (minimum transmission 45.3%). The structure was solved by direct methods (SHELXS-86). Atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least squares (unit weights, Enraf-Nonius SDP). The positions of the hydrogen atoms were found by a final Fourier synthesis and refined isotropically. R = 0.017, R_w = 0.021: reflex/parameter ratio 8.19; residual electron density +0.74/−0.65 e Å^{-3}.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft (SFB 347) and the Fonds der Chemischen Industrie for financial support. We also gratefully acknowledge support by Mrs. R. Schedl und C. P. Kneis (elemental analysis and DTA), Mrs. M. L. Schäfer and B. Stempfle (NMR spectra), and Degussa AG (chemicals).

Supplementary Material Available: Tables of crystal data, bond lengths and angles, positional and thermal parameters, and least-squares planes and a molecular structure drawing for 8 (8 pages). Ordering information is given on any current masthead page.

OM9308203