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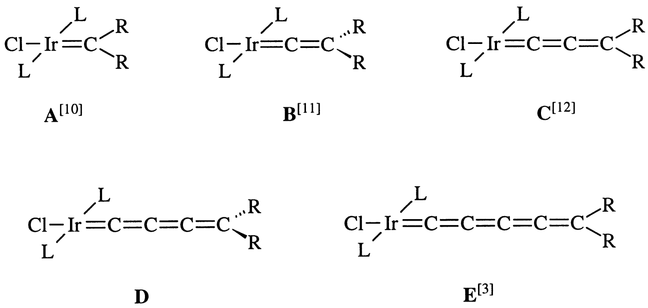
# The First Structurally Characterized Metal Complex with the Molecular Unit $M{=}C{=}C{=}C{=}CR_2$**

Kerstin Ilg and Helmut Werner*

*Dedicated to Professor Henri Brunner*
*on the occasion of his 65th birthday*

The chemistry of metallacumulenes of the general composition $[L_xM{=}C({=}C)_nRR']$, which could be considered as near relatives of metal carbenes, continues to receive a great deal of attention. While species with $n = 1$ and 2 have already been extensively investigated,[1] not too much is known about the compounds with $n = 3$ and 4. In 1994, Dixneuf and co-workers reported the synthesis of the first cationic complex with $Ru{=}C{=}C{=}C{=}C{=}CPh_2$ as the building block,[2] and a few months later we described the isolation of the first neutral compound with $Ir{=}C{=}C{=}C{=}C{=}CPh_2$ as the core unit.[3] In the meantime, the field of metallahexapentaenes $[L_xM{=}C({=}C)_4RR']$ has further been developed, mainly due to the work by Fischer et al.[4]

Earlier attempts to prepare *metallapentatetraenes*, that is compounds with $n = 3$ in the above-mentioned formula, date back to Lomprey and Selegue[5] and somewhat later to Bruce and co-workers.[6] The latter group, by using $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2(thf)]PF_6$ and buta-1,3-diyne as the starting materials, generated in situ a cationic complex containing the fragment $Ru{=}C{=}C{=}C{=}CH_2$ and supported the existence of this species by trapping reactions with nucleophiles such as $NHPh_2$, $PPh_3$, $H_2O$, and imines. More recently, both the groups of Dixneuf[7] and Winter[8] reported about the in situ formation of cationic intermediates with the molecular unit $Ru{=}C{=}C{=}C{=}CHR$ and revealed that these can be converted to corresponding acylvinylidene, acylalkynyl, butenynyl, and allenylidene ruthenium derivatives. In 1999, a dinuclear cationic compound with the core fragment $[M]{=}C{=}C{=}C{=}CH[M']$ ($[M] = (\eta^5\text{-}C_5Me_5)Fe('P_2')$, $'P_2' =$ 1,2-bis(diphenylphosphanyl)ethane (dppe), 1,2-bis(diisopropylphosphanyl)ethane (dippe); $[M'] = (\eta^5\text{-}C_5Me_5)Fe(CO)_2)$) was prepared by Lapinte and co-workers, using the butadiynediyl complex $[M]C{\equiv}CC{\equiv}C[M']$ as the precursor.[9] We have now succeeded with the isolation and structural characterization of the first stable neutral compound of the type $[L_xM{=}C{=}C{=}C{=}CR_2]$ with $L_xM = IrCl(PiPr_3)_2$, which fills the gap in the system of the metallacumulenes **B**–**E** ($L = PiPr_3$).



**A**[10] **B**[11] **C**[12]

**D** **E**[3]

$L = PiPr_3$

The synthetic route for the iridium complex of type **D** follows the methodology which we used for the corresponding allenylidene derivatives *trans*-$[IrCl({=}C{=}C{=}CRR')(PiPr_3)_2]$.[11d, 12] Since the $C_3$ ligand in the compounds of type **C** was generated from propargylic alcohols $HC{\equiv}CCRR'OH$, for the preparation of a species with a homologous $C_4$ unit we had to find a precursor with an additional carbon atom in the $C_n$ chain. The best choice seemed to be the ethynyl ketone $HC{\equiv}CC(O)CHPh_2$.[13] On reaction of this substrate with the dihydride **1**, the alkynyl(hydrido) complex **2** is formed which, however, is unstable in solution and isomerizes to the corresponding vinylidene derivative **3**. The existence of **2** can be confirmed by trapping the intermediate with pyridine, which results in the formation of the octahedral complex **4**. In contrast to the $^1H$ NMR spectrum of **3**, those of **2** and **4** display a triplet resonance in the high-field region at $\delta = -40.96$ (for **2**) and $-21.68$ (for **4**), the chemical shift of which is

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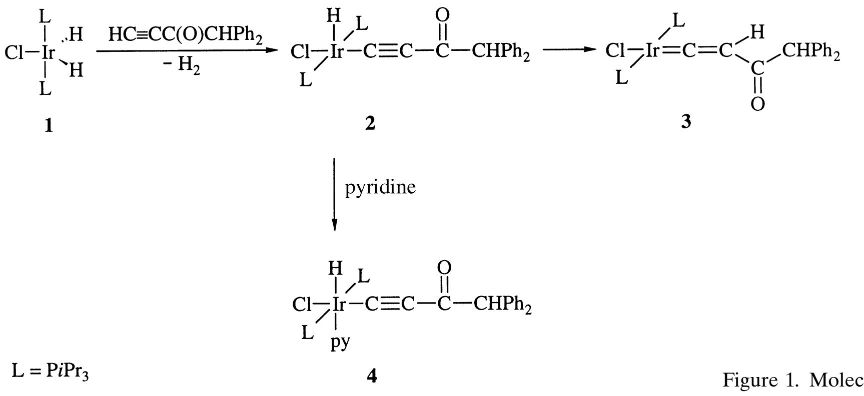
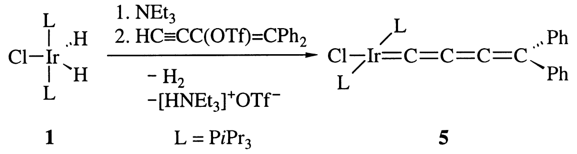


characteristic for five- and six-coordinate hydridoiridium(III) complexes, respectively.[14]

In reactions in which **2** or **3** are used as the starting material, the elimination of water can be induced neither by base nor by acid catalysis. Therefore, it was necessary to bind a better leaving group to the $\gamma$-carbon atom of the substrate and at the same time to shift the keto–enol equilibrium to the side of the enol. Attempts to convert the keto function in the coordination sphere of the complex to the corresponding enol ester by using $(CF_3SO_2)_2O$ in the presence of 4-dimethylaminopyridine led only to the decomposition of the starting material **2**. The key to success was the use of the functionalized 1-alkyne $HC{\equiv}CC(OTf){=}CPh_2$[15] (Tf = $F_3CSO_2$), which reacts with **1** in hexane even at −100 °C in the presence of one equivalent of triethylamine. The reaction is accompanied both by an evolution of gas and by a change of color from yellow to olive. After separation of the ammonium salt and recrystallization of the crude product from acetone, the butatrienylidene complex **5** is isolated as an olive-green, moderately air-sensitive solid in 77 % yield. With respect to the color, we note that a solution of **5** in benzene appears red.



The presence of a cumulated $C_4$ chain in **5** is indicated both by the IR spectrum, which displays an absorption at 1993 cm$^{-1}$, and by the $^{1}$H NMR spectrum, which shows a splitting pattern for the signals of the phenyl protons that is typical for a system with a rotational symmetry around the Ir–$C_4$ axis. The $^{13}$C NMR spectrum of **5** displays four triplet resonances for the carbon atoms of the cumulene moiety, the assignment of which is supported by the size of the $^{13}$C–$^{31}$P coupling constant. The proposed structure of **5** was finally confirmed by a single-crystal X-ray structure analysis (Figure 1).[16] The unsaturated carbon chain is nearly linear and deviates only weakly at C1 from the ideal value of 180°. The bond length Ir–C1 is 1.816(1) Å and thus somewhat shorter than the Ir–C bond lengths in *trans*-$[IrF({=}C{=}C{=}CPh_2)(PiPr_3)_2]$ (1.853(19) Å)[12] and *trans*-$[IrCl({=}C{=}C{=}C{=}C{=}CPh_2)(PiPr_3)_2]$ (1.834(5) Å).[3] The lengths of the two internal C–C double bonds are almost identical (1.283(8) Å and 1.275(8) Å), whereas the terminal bond C3–C4 is slightly longer (1.339(8) Å).

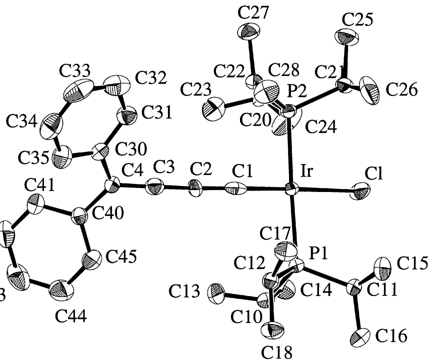
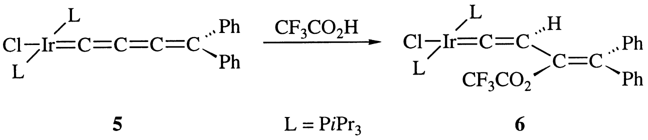


Figure 1. Molecular structure of **5** in the crystal. Selected bond lengths [Å] and angles [°]: Ir-C1 1.816(6), C1-C2 1.283(8), C2-C3 1.275(8), C3-C4 1.339(8), Ir-P1 2.350(1), Ir-P2 2.356(1); P1-Ir-P2 177.82(5), Cl-Ir-C1 172.9(2), P1-Ir-C1 90.0(2), P2-Ir-C1 90.7(2) Ir-C1-C2 175.1(5), C1-C2-C3 178.1(6), C2-C3-C4 178.7(7).

To receive a first hint about the reactive centers of the neutral butatrienylidene compound **5**, we treated this species with $CF_3CO_2H$ and isolated the vinylvinylidene complex **6**. Evidently, instead of an attack of the proton at the nucleophilic metal center a regioselective addition of HX at the $C_\beta{=}C_\gamma$ bond takes place. Therefore, the reactivity of the neutral compound **5** differs from that of the above-mentioned cations with the core fragment $Ru{=}C{=}C{=}C{=}CH_2$, which upon treatment with protic nucleophiles afford methyl-substituted allenylidene complexes by addition of HX at the $C_\gamma{=}C_\delta$ bond.[6a,c]



### *Experimental Section*

**2**: A solution of **1**[13a] (113 mg, 0.22 mmol) in hexane (15 mL) was treated at −78 °C with $HC{\equiv}CC(O)CHPh_2$ (48 mg, 0.22 mmol). After the mixture had been warmed to room temperature, the solvent was evaporated and the beginning crystallization was completed at −78 °C. The red microcrystalline solid was separated from the mother liquor and dried in vacuo; yield: 150 mg (90 %); m.p. 96 °C (decomp); IR ($C_6H_6$): $\tilde{\nu}$ = 2310 (IrH), 2062 (C≡C), 1683 cm$^{-1}$ (C=O); $^{1}$H NMR (200 MHz, $C_6D_6$)[16]: $\delta$ = 7.42 (m, *ortho*-H of $C_6H_5$), 7.08 (m, *meta*- and *para*-H of $C_6H_5$), 5.34 (s, C*H*Ph$_2$), 2.89 (m, PC*H*CH$_3$), 1.15 (dvt, *N* = 14.2, $^{3}J$(H,H) = 7.1 Hz, PCHC*H*$_3$), 1.07 (dvt, *N* = 14.5, $^{3}J$(H,H) = 7.3 Hz, PCHC*H*$_3$), −40.96 (t, $^{2}J$(P,H) = 11.6 Hz, IrH); $^{31}$P{$^{1}$H} NMR (81.0 MHz, $C_6D_6$): $\delta$ = 39.2 (s).

**3**: A solution of **2** (62 mg, 0.08 mmol) in benzene (10 mL) was stirred for 3 h at room temperature. After removal of the solvent the residue was suspended in pentane (2 mL) and the suspension was stored for 12 h at −78 °C. The red-violet solid was separated from the mother liquor and dried in vacuo; yield: 57 mg (92 %); m.p. 142 °C (decomp); IR (KBr): $\tilde{\nu}$ = 1654 (C=O), 1544 cm$^{-1}$ (C=C); $^{1}$H NMR (200 MHz, $C_6D_6$): $\delta$ = 7.30 (m, *ortho*-H of $C_6H_5$), 7.06 (m, *meta*- and *para*-H of $C_6H_5$), 4.84 (s, C*H*Ph$_2$), 2.78 (m, PC*H*CH$_3$), 1.28 (dvt, *N* = 14.5, $^{3}J$(H,H) = 7.3 Hz, PCHC*H*$_3$), −1.45 (t, $^{4}J$(P,H) = 2.9 Hz, =C*H*); $^{13}$C{$^{1}$H} NMR (50.3 MHz, $C_6D_6$): $\delta$ = 255.2 (t, $^{2}J$(P,C) = 11.6 Hz, Ir=*C*=C), 181.3 (s, CO), 140.9 (s, *ipso*-$C_6H_5$), 129.6, 128.4, 126.9 (all s, $\mathrm{C_6H_5}$), 112.4 (t, $^3J$(P,C) = 3.5 Hz, $\mathrm{Ir{=}C{=}\mathit{C}}$), 64.3 (s, $\mathrm{\mathit{C}HPh_2}$), 23.5 (vt, $N$ = 26.8 Hz, $\mathrm{P\mathit{C}HCH_3}$), 20.1 (s, $\mathrm{PCH\mathit{C}H_3}$); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (81.0 MHz, $\mathrm{C_6D_6}$): $\delta = 37.1$ (s).

**4**: A solution of **2** (66 mg, 0.09 mmol) in diethyl ether (10 mL) was treated with pyridine (7 µL, 0.09 mmol) and stirred for 5 min at room temperature. After removal of the solvent, the off-white residue was dissolved in refluxing hexane (2 mL) and the solution then cooled to −78 °C. The resulting microcrystalline solid was separated from the mother liquor and dried in vacuo; yield: 67 mg (93 %); m.p. 127 °C (decomp); IR (KBr): $\tilde{\nu}$ = 2252 (IrH), 2054 (C≡C), 1620 cm$^{-1}$ (C=O); $^1$H NMR (400 MHz, $\mathrm{C_6D_6}$): $\delta$ = 10.24, 9.90 (both br s, *ortho*-H of $\mathrm{C_5H_5N}$), 7.49 (m, *ortho*-H of $\mathrm{C_6H_5}$), 7.05 (m, *meta*- and *para*-H of $\mathrm{C_6H_5}$), 6.82 (m, *para*-H of $\mathrm{C_5H_5N}$), 6.56 (m, *meta*-H of $\mathrm{C_5H_5N}$), 5.43 (s, $\mathrm{C\mathit{H}Ph_2}$), 2.84 (m, $\mathrm{PC\mathit{H}CH_3}$), 1.06 (dvt, $N$ = 14.0, $^3J$(H,H) = 7.3 Hz, $\mathrm{PCHC\mathit{H}_3}$), 1.01 (dvt, $N$ = 14.0, $^3J$(H,H) = 7.3 Hz, $\mathrm{PCHC\mathit{H}_3}$), −21.68 (t, $^2J$(P,H) = 16.0 Hz, IrH); $^{13}$C NMR (100.6 MHz, $\mathrm{C_6D_6}$): $\delta$ = 182.3 (s, CO), 140.8 (s, *ipso*-$\mathrm{C_6H_5}$), 154.9, 152.3, 136.7, 129.7, 129.4, 128.5, 128.3, 126.7 (all s, $\mathrm{C_6H_5}$ and $\mathrm{C_5H_5N}$), 110.8 (t, $^3J$(P,C) = 4.1 Hz, $\mathrm{IrC{\equiv}\mathit{C}}$), 67.1 (s, $\mathrm{\mathit{C}HPh_2}$), 23.8 (vt, $N$ = 26.4 Hz, $\mathrm{P\mathit{C}HCH_3}$), 19.2, 19.1 (both s, $\mathrm{PCH\mathit{C}H_3}$), resonance of $\mathrm{Ir\mathit{C}{\equiv}C}$ not observed; $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (162.0 MHz, $\mathrm{C_6D_6}$): $\delta = 10.4$ (s).

**5**: A solution of **1** (110 mg, 0.22 mmol) in hexane (15 mL) was treated at −100 °C with $\mathrm{NEt_3}$ (24 µL, 0.22 mmol) and subsequently with a solution of $\mathrm{HC{\equiv}CC(OTf){=}CPh_2}$ (77 mg, 0.22 mmol) in hexane (20 mL). After the reaction mixture had been warmed to room temperature, the solvent was evaporated, the residue was extracted with pentane (30 mL), and the extract was evaporated to dryness in vacuo. Recrystallization from acetone at −78 °C yielded an olive-green solid which was dried in vacuo; yield: 123 mg (77 %); m.p. 62 °C (decomp); IR (KBr): $\tilde{\nu}$ = 1993 cm$^{-1}$ (C=C=C=C); $^1$H NMR (400 MHz, $\mathrm{C_6D_6}$): $\delta$ = 7.50 (m, *ortho*-H of $\mathrm{C_6H_5}$), 7.21 (m, *meta*-H of $\mathrm{C_6H_5}$), 6.82 (m, *para*-H of $\mathrm{C_6H_5}$), 2.89 (m, $\mathrm{PC\mathit{H}CH_3}$), 1.28 (dvt, $N$ = 13.8, $^3J$(H,H) = 7.0 Hz, $\mathrm{PCHC\mathit{H}_3}$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (100.6 MHz, $\mathrm{C_6D_6}$): $\delta$ = 255.7 (t, $^2J$(P,C) = 13.7 Hz, $\mathrm{Ir{=}\mathit{C}{=}C{=}C{=}C}$), 174.6 and 164.1 (both t, $^3J$(P,C) = $^4J$(P,C) = 3.6 Hz, $\mathrm{Ir{=}C{=}\mathit{C}{=}C{=}C}$ and $\mathrm{Ir{=}C{=}C{=}\mathit{C}{=}C}$), 132.1 (s, *ipso*-$\mathrm{C_6H_5}$), 130.2, 128.5, 127.3 (all s, $\mathrm{C_6H_5}$), 105.9 (t, $^5J$(P,C) = 2.5 Hz, $\mathrm{Ir{=}C{=}C{=}C{=}\mathit{C}}$), 23.6 (vt, $N$ = 26.4 Hz, $\mathrm{P\mathit{C}HCH_3}$), 20.1 (s, $\mathrm{PCH\mathit{C}H_3}$); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (162.0 MHz, $\mathrm{C_6D_6}$): $\delta = 26.7$ (s).

**6**: A solution of **5** (53 mg, 0.07 mmol) in benzene (5 mL) was treated with $\mathrm{CF_3CO_2H}$ (5.5 µL, 0.07 mmol) at room temperature and the resulting red-violet solution stirred for 5 min. The solvent was removed in vacuo and the residue recrystallized from pentane (2 mL) at −60 °C; red-violet crystals; yield: 52 mg (87 %); m.p. 106 °C (decomp); IR (KBr): $\tilde{\nu}$ = 1795 $\mathrm{(OCO)_{as}}$, 1626 (C=C), 1457 cm$^{-1}$ $\mathrm{(OCO)_{sym}}$; $^1$H NMR (200 MHz, $\mathrm{C_6D_6}$): $\delta$ = 7.27 (m, *ortho*-H of $\mathrm{C_6H_5}$), 6.93 (m, *meta*-H of $\mathrm{C_6H_5}$), 2.88 (m, $\mathrm{PC\mathit{H}CH_3}$), 1.28 (dvt, $N$ = 13.4, $^3J$(H,H) = 6.7 Hz, $\mathrm{PCHC\mathit{H}_3}$), −2.81 (t, $^4J$(P,H) = 2.1 Hz, $\mathrm{{=}C\mathit{H}}$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (50.3 MHz, $\mathrm{C_6D_6}$): $\delta$ = 255.6 (t, $^2J$(P,C) = 12.1 Hz, $\mathrm{Ir{=}\mathit{C}{=}C}$), 154.6 (q, $^2J$(F,C) = 43.2 Hz, $\mathrm{CF_3\mathit{C}O_2}$), 148.1 (br s, $\mathrm{\mathit{C}(O_2CCF_3){=}CPh_2}$), 140.0, 138.8, 130.2, 129.3, 123.3, 120.2 (all s, $\mathrm{C_6H_5}$), 138.7 (s, $\mathrm{{=}\mathit{C}Ph_2}$), 115.3 (q, $^1J$(F,C) = 268.0 Hz, $\mathrm{\mathit{C}F_3CO_2}$), 104.9 (t, $^3J$(P,C) = 3.8 Hz, $\mathrm{Ir{=}C{=}\mathit{C}}$), 23.4 (vt, $N$ = 26.7 Hz, $\mathrm{P\mathit{C}HCH_3}$), 20.0 (s, $\mathrm{PCH\mathit{C}H_3}$); $^{19}\mathrm{F}\{^1\mathrm{H}\}$ NMR (188.0 MHz, $\mathrm{C_6D_6}$): $\delta = -74.4$ (s); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (162.0 MHz, $\mathrm{C_6D_6}$): $\delta = 32.2$ (s).

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[16] Crystal structure analysis of **5**: Crystals from diethyl ether at 5 °C, $\mathrm{C_{34}H_{52}ClIrP_2}$ (750.35); crystal dimensions 0.21 × 0.20 × 0.05 mm; triclinic, space group $P\bar{1}$ (no.2), $a = 8.7412(17)$, $b = 12.309(2)$, $c = 16.213(3)$ Å, $\alpha = 96.425(12)$, $\beta = 91.125(13)$, $\gamma = 103.352(11)°$, $Z = 2$, $V = 1684.8(6)$ Å$^3$, $\rho_{\mathrm{calcd}} = 1.479$ g cm$^{-3}$; $T = 193(2)$ K; $2\Theta = 45°$; 4931 reflections measured; 4391 were unique ($R_{\mathrm{int}} = 0.0260$), and 3947 observed ($I > 2\sigma(I)$); Enraf-Nonius-CAD4 diffractometer, $\mathrm{Mo_{K\alpha}}$ radiation ($\lambda = 0.71073$ Å), graphite monochromator, zirconium filter (factor 15.2); Lp- and empirical absorption correction ($\Psi$ scan, min. transmission 67.21 %). The structure was solved by Patterson method, refinement with full-matrix, least-squares method; $R_1 = 0.0277$, $wR_2 = 0.0627$ (for 3947 reflections with $I > 2\sigma(I)$), $R_1 = 0.0346$, $wR_2 = 0.0667$ (for all 4391 data); data-to-parameter ratio 12.37; residual electron density +1.015/−0.919 e Å$^{-3}$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-138491. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[17] Abbreviations: v = virtual triplet, dvt = doublet of virtual triplets, $N = {}^3J(\mathrm{P,H}) + {}^5J(\mathrm{P,H})$ or ${}^1J(\mathrm{P,C}) + {}^3J(\mathrm{P,C})$.