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Preliminary Communication

Organometallic compounds of iridium and rhodium

XXXII *. (Trimethylsilyl)diazomethyl derivatives of [^{t}BuP($CH_2CH_2CH_2PPh_2$)$_2$]MCl (M = Rh, Ir)

Lutz Dahlenburg and Markus Ernst

Institut für Anorganische Chemie, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstraße 1, D-91058 Erlangen (Germany)

Michèle Dartiguenave and Yves Dartiguenave

Laboratoire de Chimie Inorganique, Université P. Sabatier, 118 route de Narbonne, F-31062 Toulouse-Cedex (France)

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Abstract

Treatment of [^{t}BuP($CH_2CH_2CH_2PPh_2$)$_2$]MCl (M = Rh, **1**, or Ir, **2**) with LiC(N_2)SiMe_3 in toluene at −78°C gave the α-diazoalkyl complexes [^{t}BuP($CH_2CH_2CH_2PPh_2$)$_2$]RhC(N_2)SiMe_3, **3**, and [^{t}BuP($CH_2CH_2CH_2PPh_2$)$_2$]IrC(N_2)SiMe_3, **4**, as air- and light-sensitive but thermally stable compounds, which were characterized by IR, ^{1}H NMR and ^{31}P NMR spectroscopy. The results of an X-ray structural study of complex **2** are also reported.

Complexes containing diazoalkyl ligands C-bonded to a transition metal, $L_nMC(N_2)R$, are of particular interest as precursors for compounds with metal-to-carbon multiple bonds [3]. Yet, their chemistry remains quite undeveloped because reasonably stable examples are still few in number, and have so far been limited to some derivatives of palladium [4], osmium [5], rhodium [6], and nickel [7]. Detailed investigations of the (R_3P)$_n$RhCl/LiC(N_2)SiMe_3 system (R = Me, $n = 4$; R = Et, $n = 3$) have shown that the thermal stability of the α-diazoalkyl product, (R_3P)$_n$RhC(N_2)SiMe_3, appears to depend crucially on the nature of the ancillary phosphine attached to the central metal. Thus whereas the PMe_3 complex decomposed in the solid state and so was characterized only in solution [6a,d], the PEt_3 derivative [6c–e] was isolated as a crystalline solid, stable at ambient temperature. In addition, it was observed that rhodium(I) complexes such as (Ph_3P)$_3$-RhCl with sterically more demanding and, simultaneously, less basic phosphine ligands than PMe_3 or PEt_3, did not form any α-diazoalkyl derivative when treated with LiC(N_2)SiMe_3 [6d].

These observations prompted us to study the synthesis of thermally stable C-metallated 16e diazoalkyl complexes of rhodium and iridium from L_3MCl precursors containing a chelating tridentate phosphine ligand; *e.g.*, ^{t}BuP($CH_2CH_2CH_2PPh_2$)$_2$, which was previously shown to form the well characterized rhodium(I) complex [^{t}BuP($CH_2CH_2CH_2PPh_2$)$_2$]RhCl, **1** [8]. The iridium homologue of **1**, [^{t}BuP($CH_2CH_2CH_2PPh_2$)$_2$]IrCl, **2**, was prepared from Ir_2Cl_2 (*cyclo*-C_8H_{14})$_4$ and the tris(phosphine) under carefully controlled conditions in toluene/hexane in the cold [9*], and was fully characterized by NMR spectroscopy (in C_7D_8: $\delta(P^{t}Bu) = -0.42$, $\delta(PPh_2) = -9.63$, $J(PP) = 30.0$ Hz) and single-crystal X-ray diffraction; Fig. 1 [10*].

Trimethylsilyldiazomethyl derivatives of **1** and **2** were obtained by adding a solution of the α-lithiodiazo compound LiC(N_2)SiMe_3 [11] in toluene (2.2 equiv.) to a toluene solution of the relevant chloro-rhodium or -iridium complex at −78°C. The mixture was allowed to warm slowly to room temperature and the solution then filtered through Celite. Removal of the solvent, extraction with diethyl ether, and concentration, gave analytically pure orange crystals of the products, [^{t}BuP($CH_2CH_2CH_2PPh_2$)$_2$]RhC(N_2)SiMe_3, **3**, and [^{t}BuP($CH_2CH_2CH_2PPh_2$)$_2$]IrC(N_2)SiMe_3, **4**, in yields of 69% and 62%, respectively (**3**: C, 59.6; H, 7.1; N, 3.4; $C_{38}H_{50}N_2P_3RhSi$ (758.74) calcd.: C, 60.15; H, 6.64; N, 3.69%. **4**: C, 53.6; H, 6.1; N, 3.1; $C_{38}H_{50}IrN_2P_3Si$ (848.05) calcd.: C, 53.82; H, 5.94; N, 3.30%). The success of these preparations depended on the avoidance of polar solvents for the initial reactions, since

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Correspondence to: Prof. Dr. L. Dahlenburg.

* For Part XXXI see Ref. 1. This paper is also Part XXXIX of "Oligophosphine ligands" (for Part XXXVIII see Ref. 2).

* Reference number with asterisk indicates a note in the list of references.

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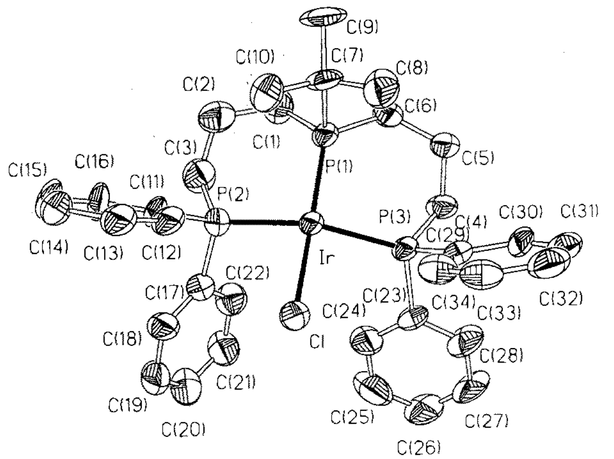

Fig. 1. Structure of [^{t}BuP(CH$_2$CH$_2$CH$_2$PPh$_2$)$_2$]IrCl; selected bond lengths (Å) and angles (deg): Ir–Cl, 2.404(6); Ir–P(1), 2.212(6); Ir–P(2), 2.280(7); Ir–P(3), 2.288(6); Cl–Ir–P(1), 166.4(2); Cl–Ir–P(2), 88.0(2); Cl–Ir–P(3), 88.8(2); P(1)–Ir–P(2), 94.0(2); P(1)–Ir–P(3), 94.8(2); P(2)–Ir–P(3), 155.3(2).

unseparable mixtures of products are obtained if solvents such as THF or Et_2O are employed as reaction media.

Though very air- and light-sensitive, both **3** and **4** are thermally stable up to at least 40°C *in vacuo*. The spectroscopic properties are in agreement with the expected structure. In the infrared (Nujol mull), the compounds display one sharp $\nu(CN_2)$ absorption, at 1952 cm^{-1} (**3**) and 1955 cm^{-1} (**4**), characteristic of the C-coordinated diazomethyl ligand [6a,d,e]. The ^{31}P NMR spectra, obtained in C_7D_8 at 145.79 MHz, exhibit the anticipated patterns: AM_2X ($A = P^tBu$, $M = PPh_2$; $X = {}^{103}Rh$) with $\delta(A) = 22.41$, $\delta(B) = 9.60$, $J_{AM} = 45.6$, $J_{AX} = 128.7$, and $J_{MX} = 149.2$ Hz for **3**, and A_2M ($A = PPh_2$, $M = P^tBu$) with $\delta(A) = 1.35$, $\delta(M) = -0.77$, and $J_{AM} = 27.8$ Hz for **4**. Selected ^1H NMR data (C_6D_6 or C_7D_8) are: $\delta = 0.23$ (s, 9H; $SiMe_3$) and $\delta = 1.25$ (d, 9H; $PCMe_3$; $J(PH) = 12.3$ Hz) (compound **3**) as well as $\delta = 0.22$ (s, 9H; $SiMe_3$) and $\delta = 1.31$ (d, 9H; $PCMe_3$; $J(PH) = 12.6$ Hz) (compound **4**). At low temperature there is restricted rotation of the trimethylsilyl group about the C–Si bond, as indicated by the appearance of two singlets at $\delta = 0.21$ (6 H) and $\delta = 0.38$ (3 H) in the ^1H NMR spectrum of **3** at 225 K.

The overall molecular geometry of the two compounds was confirmed by the preliminary results of an X-ray structure analysis performed on single crystals of the rhodium derivative **3**, which show that the CMe_3 and $SiMe_3$ substituents on the phosphine and the diazoalkyl ligands occupy mutually *trans* positions with respect to the molecular plane. However, as found previously for $(Et_3P)_3RhC(N_2)SiMe_3$ [6d,e], full refinement of the structure was frustrated by the rapid deterioration of crystals of **3** in the X-ray beam, and more detailed discussion would not be appropriate at present [12*].

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9 Reactions at ambient temperature produced almost colourless orthometallated Ir^{III} products rather than orange complex **1**.

10 Crystal data: from single-crystal diffractometry (Syntex $P2_1$) with Mo Kα radiation ($\lambda = 0.71069$ Å) at 20 ± 2°C; monoclinic $P2_1/n$; $a = 13.464(7)$, $b = 17.568(12)$, $c = 14.370(10)$ Å, $\beta = 107.09(5)°$; $V = 3248$ Å^3; $Z = 4$, mol. wt. 770.29 ($C_{34}H_{41}ClIrP_3$); $D_{calcd} = 1.58$ g cm^{-3}. Data collection: $\theta/2\theta$ scan mode; 6230 data collected ($4.5° \leq 2\theta \leq 50°$), 5752 unique, 4112 used ($|F_o| > 4\sigma$); uncorrected for absorption (μ(Mo Kα) = 41.8 mm^{-1}). Structure solution and refinement: Patterson, difference Fourier, and block-diagonal least-squares methods employing Sheldrick's SHELXS-86 and SHELX-76 program systems with scattering factors from the sources given therein; anisotropic thermal parameters for all non-hydrogen atoms; hydrogens not included; $R = 0.079$, $R_w = 0.083$ (unit weights); Supplementary material has been deposited at the Fachinformationszentrum Karlsruhe (cooperating with the Cambridge Crystallographic Data Centre), D-76344 Eggenstein-Leopoldshafen. Any request should be accompanied by the registration number CSD-57259 as well as by the full literature citation for this communication.

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12 Crystal data: from single-crystal diffractometry (Enraf-Nonius CAD4) with Mo Kα radiation ($\lambda = 0.71069$ Å) at 20 ± 2°C; monoclinic $P2_1/c$; $a = 19.010(6)$, $b = 11.537(5)$, $c = 19.247(4)$ Å, $\beta = 103.84(2)$°; $V = 4099$ Å^3; $Z = 4$, mol. wt. 758.74 ($C_{38}H_{50}N_2P_3$-RhSi); $D_{calcd} = 1.23$ g cm^{-3}; μ(Mo Kα) = 0.52 mm^{-1}). Data collection: ω scan mode; 6289 data collected ($2° \leq 2\theta \leq 48°$), 1703 significant ($I > 3\sigma$); 170 parameters refined; current R: 0.133 (too many bad reflections).