Transformation of a Platinum Carbonyl into a Platinum Carbene Moiety by Reaction with (η⁴-Butadiene)zirconocene

Gerhard Erker* and Babil Menjón[+]

Institut für Organische Chemie der Universität Würzburg,
Am Hubland, D-8700 Würzburg, F.R.G.

While (η⁴-butadiene)zirconocene and -hafnocene do not react with $Pt(PPh_3)_2(CO)_2$ (**2**) in toluene solution at room temperature, $cp_2Zr(η^4-C_4H_6)$ (**1a**: cp = $η^5-C_5H_5$; **1b**: cp = $η^5-C_5H_4CH_3$) reacts with $cis-Pt(C_6F_5)_2L(CO)$ (**3**: L = CO; **5**: L = PiPr_3) under similar conditions to give the metallacyclic Fischer-type car-

bene complexes $cp_2ZrOC[=Pt(C_6F_5)_2L]C_4H_6$ (**4**: L = CO; **6**: L = PiPr_3). When L = CO, isomerization takes place by UV irradiation ($cis-4 \rightleftharpoons trans-4$) presumably as the result of a dissociative CO scrambling process. This is not observed when L = PiPr_3.

Introduction

The hydro- or carbometalation of a C≡O bond in metal carbonyl complexes has been shown to be a general way of synthesizing heteroatom-stabilized carbene complexes[1]. This procedure is especially useful in cases where the method of transforming a metal carbonyl into a metal carbene moiety originally developed by Fischer et al.[2] is not applicable.

Despite the large number of palladium(II) and platinum(II) carbene complexes known, to the best of our knowledge none of them has been prepared starting from a metal carbonyl precursor[3]. Fischer's method has, in fact, been applied to the conversion of group-10 metal carbonyl complexes with rather restricted success. Thus, it appears that only $Ni(CO)_4$ has been reported to yield carbene complexes and even these of very limited stability[4,5]. As already pointed out[1], the reason for this could be the inherent instability of the acyl nickelate anions obtained by nucleophilic attack on $Ni(CO)_4$[6] and needed for the subsequent reaction with an electrophile. On the other hand, the analogous palladium and platinum binary carbonyls are too instable on their own for carrying out a thorough study of the metal carbonyl → metal carbene conversion[7]. Remarkably, no zerovalent heteroatom-stabilized palladium or platinum carbene complexes seem to have been reported so far[3] despite of the availability of various potential starting materials containing ancillary ligands other than CO.

On going to the oxidation state II, the availability of carbonyl complexes is altered, the more stable ones now being those of platinum[8]. Nucleophilic attack on $cis-PtCl_2(CO)_2$ or a number of cationic monocarbonyl compounds of platinum(II) renders alkoxycarbonyl or carboxamido derivatives, sufficiently stable to be isolated and to withstand further electrophilic attack[9,10]. A similar behavior is observed in the chemistry of palladium(II), where the isolation of the metal carbonyl precursors — usually of rather limited stability — is even not needed[11].

On these grounds, the possibility of effecting the conversion of a platinum carbonyl into a platinum carbene moiety by means of the (η⁴-butadiene)zirconocene reagent seemed to be of interest. To achieve this transformation we have chosen $Pt(PPh_3)_2(CO)_2$[12] and

$cis-Pt(C_6F_5)_2(CO)_2$[13] as suitable starting materials because of their high stability; the results obtained are reported in this paper.

Results and Discussion

A [D_6]benzene solution of $(η^5-C_5H_5)_2Zr(η^4-C_4H_6)$ (**1**) — available as an ($s-cis/s-trans-η^4$-diene)metallocene equilibrium mixture[14] — does not react at room temperature with the dicarbonyl derivative of platinum(0), $Pt(PPh_3)_2(CO)_2$ (**2**), nor does the analogous $(η^5-C_5H_5)_2Hf(η^4-C_4H_6)$[15], as monitored by ¹H-NMR spectroscopy. The failure of **2** to react may be due to steric factors. Thus, the tetrahedral coordination geometry of the platinum center[16] together with the steric requirements of the two PPh_3 ligands could well hinder the initial π coordination of a CO group to the reactive unsaturated $(η^2-butadiene)metallocene$ species. In addition, zerovalent platinum seems not to be able to stabilize the carbene fragment as derived from the fact that no carbene complexes of platinum(0) have been synthesized so far[3].
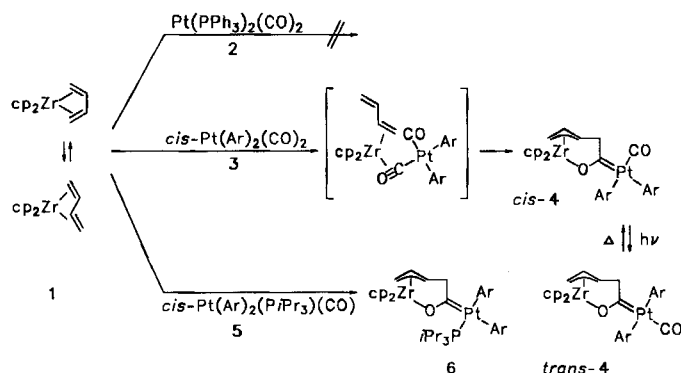
a: cp = η-C₅H₅; b: η-C₅H₄CH₃.— Ar = C₆F₅

Conversely, the square-planar dicarbonyl complex of platinum(II), $cis-Pt(C_6F_5)_2(CO)_2$ (**3**), readily reacts with **1** (**a**: cp = $η^5-C_5H_5$; **b**: cp = $η^5-C_5H_4CH_3$) in toluene solution at room temperature to give **4**. The total consumption of the dicarbonyl precursor **3** can easily be followed by IR spectroscopy. The characteristic v(CO) pattern of **3** (2174, 2143 cm⁻¹)[13] disappears, and a single

band at lower frequency (4a: 2083 cm^{-1}; 4b: 2082 cm^{-1}) is observed instead. This implies that the zirconoxycarbene fragment acts as a stronger σ donor and a poorer π acceptor than the original CO ligand[17]. When the reaction is carried out in [D$_6$]benzene solution, 4 is the only product observed by ^{1}H- and ^{13}C-NMR spectroscopy. The reaction is virtually quantitative. As a solid complex, 4 has been isolated in about 70% yield. The ^{1}H-NMR spectrum of 4 shows the typical signal pattern of the η^3-allyl unit bonded to zirconium together with two signals corresponding to the diastereotopic cp groups. The carbene ^{13}C-NMR signal is observed at $\delta = 294.9$ and 295.2 for 4a and 4b, respectively, while the signal corresponding to the carbonyl group appears at $\delta = 175.5$ for both complexes.

A remarkable feature of 4 is the photolabile character of the carbonyl group that has remained attached to the platinum center. Simply the prolonged exposure of a [D$_6$]benzene solution of 4 in a sealed NMR tube to daylight causes some signals of the original spectrum to duplicate. This effect is substantially accelerated by Pyrex-filtered UV irradiation. A possible explanation for this phenomenon is the existence of an equilibrium between two isomeric species to which we tentatively assign the geometries cis- and trans-4. A single product is observed after thermally induced ring closure[18]. UV irradiation of a sample of 4b gives a mixture, where the newly formed isomer trans-4b is the major component in the photostationary equilibrium (cis-/trans-4b = 2:3). On the other hand, UV irradiation of 4a gives an almost equimolar mixture of the two respective isomers (cis-/trans-4a = 10:9).

This isomerization could be effected by means of an intermolecular CO scrambling process. We have, therefore, replaced the photolabile CO group at platinum in 4 by a trialkylphosphine ligand. The monocarbonyl complex cis-Pt(C$_6$F$_5$)$_2$(PiPr$_3$)(CO) (5) has been synthesized by treatment of 3 with an equimolar quantity of PiPr$_3$ in toluene at room temperature[19]. This reaction proceeds straightforwardly and leads to 5 in 93% yield, isolated as a white, air-stable powder. Its IR spectrum exhibits ν(CO) at 2091 cm^{-1}, located in the range described for related monocarbonyl complexes of platinum(II)[20].

Complex 5 reacts with 1b in a similar way as its dicarbonyl precursor 3. Again, the thermally induced carbon−carbon coupling reaction yields only a single isomer, 6b, as observed by ^{1}H-, ^{13}C-, and ^{31}P-NMR spectroscopy. The IR spectrum of the reaction mixture lacks any absorption assignable to terminal carbonyl groups. After the usual workup, 6b has been isolated as a yellow solid in 74% yield.

In contrast to the photochemical behavior exhibited by 4, a [D$_8$]-tetrahydrofuran solution of 6b in a sealed NMR tube suffers no detectable changes in its ^{1}H-NMR spectrum even after prolonged UV irradiation (3 days). This result strongly supports a dissociative CO scrambling mechanism being responsible for the photochemical isomerization process observed in 4. The fact that single crystals of 4b decomposed upon exposure to X-rays may be related to the same effect. This has prevented the structure determination of complexes 4 by diffraction analysis.

Experimental

General Procedures and Materials: All reactions were carried out under argon using standard Schlenk techniques. Toluene and pentane were distilled from sodium under argon. [D$_6$]Benzene and [D$_8$]tetrahydrofuran were dried with Na/K alloy, then distilled, and stored under argon. − NMR: Bruker WP 200 SY. − IR: Nicolet 5-DXC FT. − Melting points (uncorrected): Determined in sealed glass capillaries. − Elemental analyses: Performed at the Institut für Anorganische Chemie der Universität Würzburg. − (η^5-C$_5$H$_5$)$_2$-Zr(η^4-C$_4$H$_6$)[21] (1), Pt(PPh$_3$)$_2$(CO)$_2$[12] (2), and cis-Pt(C$_6$F$_5$)$_2$(CO)$_2$[13] (3) were prepared according to literature methods.

[Carbonylbis(pentafluorophenyl)platinum]bis(cyclopentadienyl){μ-[(1,2,3-η:5-η)-5-oxo-2-pentene-1,5-diyl-O]}zirconium (4a): A mixture of 1a (0.25 g, 0.91 mmol) and 3 (0.50 g, 0.85 mmol) was dissolved in toluene (40 ml). The red solution became yellow within 20 min. Then the solution was filtered from a small amount of a brown solid. The volume of the yellow filtrate was reduced to 20 ml in vacuo and, on standing at −20°C, 0.60 g of a cream solid was obtained (4a · CH$_3$C$_6$H$_5$, 74% yield); m.p. 112°C (dec.). − IR (toluene): $\tilde{\nu}$ = 2083 cm^{-1} (C≡O). − ^{1}H NMR (200 MHz, [D$_6$]benzene): δ = 5.49, 5.34 (each s, 5H, C$_5$H$_5$), 4.68 (m, 1H, 3-H), 3.70, 2.28 (2 dd, 2H, 4-H, -H'), 1.83 (m, 2H, 1-H). − ^{13}C NMR (50.3 MHz, [D$_6$]benzene): δ = 294.9 [J(Pt,C) = 831 Hz, ZrOC=Pt], 175.4 [J(Pt,C) = 1273 Hz, CO], 151.0, 146.5, 140.0, 135.0 (4 m, C$_6$F$_5$), 114.2 (C-2), 109.3 (C$_5$H$_5$), 105.8 [J(Pt,C) = 24 Hz, C-3], 64.5 [J(Pt,C) = 170 Hz, C-4], 46.4 (C-1).

C$_{28}$H$_{16}$F$_{10}$O$_2$PtZr · CH$_3$C$_6$H$_5$ (952.86) Calcd. C 44.12 H 2.54
Found C 44.00 H 2.57

UV Irradiation of 4a: A solution of 4a (0.1 g, 0.11 mmol) in [D$_6$]benzene was irradiated in a sealed NMR tube for 3 h, after which time duplication of some signals was observed showing almost the same intensity as those corresponding to 4a (cis-/trans-4a = 10:9). Further irradiation caused no change of the relative intensities. The new signals were assigned to the isomeric species trans-4a: ^{1}H NMR (200 MHz, [D$_6$]benzene): δ = 5.36, 5.28 (2 s, C$_5$H$_5$), 3.72, 2.23 (2 dd, 4-H, -H'). − ^{13}C NMR (50.3 MHz, [D$_6$]benzene): δ = 291.6 [J(Pt,C) = 1070 Hz, ZrOC=Pt], 176.4 [J(Pt,C) = 938 Hz, CO], 114.8 (C-2), 109.4 (C$_5$H$_5$), 105.5 [J(Pt,C) = 27 Hz, C-3], 61.4 [J(Pt,C) = 213 Hz, C-4], 45.9 (C-1).

[Carbonylbis(pentafluorophenyl)platinum]bis(methylcyclopentadienyl){μ-[(1,2,3-η:5-η)-5-oxo-2-pentene-1,5-diyl-O]}zirconium (4b): This compound was obtained as described for 4a starting from 1b (0.24 g, 0.79 mmol) and 3 (0.45 g, 0.79 mmol). Addition of pentane to the reaction mixture before cooling improves the total yield. Finally, 0.43 g of yellow crystals (4b, 62% yield) was obtained; m.p. 87°C (dec.). − IR (toluene): $\tilde{\nu}$ = 2082 cm^{-1} (C≡O). − ^{1}H NMR (200 MHz, [D$_6$]benzene): δ = 5.12, 4.92 (2 m, 8H, CH$_3$C$_5$H$_4$), 4.38 (m, 1H, 3-H), 3.69, 2.19 (2 dd, 2H, 4-H, -H'), 1.65 (m, 2H, 1-H), 1.56, 1.47 (2 s, 6H, CH$_3$C$_5$H$_4$). − ^{13}C NMR (50.3 MHz, [D$_6$]benzene): δ = 295.2 [J(Pt,C) = 834 Hz, ZrOC=Pt], 175.5 [J(Pt,C) = 1268 Hz, CO], 151.2, 149.1, 145.8, 144.6, 140.3, 138.9, 135.1, 134.2 (8 m, C$_6$F$_5$), 132.9 (C-2), 123.9, 123.0 [2 s, CH$_3$C(CH$_4$)], 112.3, 110.4, 109.9, 109.6, 109.2, 107.9, 107.6, 107.3 [8 s, CH$_3$C(CH)$_4$], 105.6 [J(Pt,C) = 25 Hz, C-3], 64.5 [J(Pt,C) = 166 Hz, C-4], 47.6 (C-1), 14.4 [CH$_3$C(CH)$_4$].

C$_{30}$H$_{20}$F$_{10}$O$_2$PtZr (888.78) Calcd. C 40.54 H 2.27
Found C 40.64 H 2.52

UV Irradiation of 4b was performed as described for 4a. After irradiation for 5 h no further changes in the relative intensities of the two isomers (cis-/trans-4b = 2:3) were observed. Spectroscopic data of trans-4b: ^{1}H NMR (200 MHz, [D$_6$]benzene): δ = 5.04, 4.76 (2 m, CH$_3$C$_5$H$_4$, 2-H), 4.37 (dd, 3-H), 3.92, 2.17 (2 dd, 4-H, -H'), 1.45, 1.40 (2 s, CH$_3$C$_5$H$_4$). − ^{13}C NMR (50.3 MHz, [D$_6$]benzene): δ = 291.9 [J(Pt,C) = 1076 Hz, ZrOC=Pt], 176.1 [J(Pt,C) = 942 Hz, CO], 133.1 (C-2), 121.4 [2 s, CH$_3$C(CH)$_4$], 112.0, 111.7, 110.8, 110.6,

108.5, 106.7, 106.2, 105.8 [8 s, $CH_3C(CH)_4$], 105.4 (C-3)[22], 61.4 [J(Pt,C) = 214 Hz, C-4], 47.4 (C-1), 14.0, 13.9 [2 s, $CH_3C(CH)_4$].

cis-Carbonylbis(pentafluorophenyl)(triisopropylphosphine)-platinum (5): The addition of $PiPr_3$ (0.23 ml, 1.10 mmol) to a suspension of **3** (0.60 g, 1.02 mmol) in toluene (20 ml) caused a white solid to be formed. Evolution of a gas, presumably carbon monoxide, was observed. The colorless solution was evaporated to dryness and the white solid obtained washed with pentane (3 × 10 ml), yielding 0.72 g (93%) of **5**; m.p. 180 °C (dec.). − IR (toluene): $\tilde{v}$ = 2091 cm^{-1} (C≡O). − ^{1}H NMR (200 MHz, [D_6]benzene): δ = 1.76 [m, 1 H, CH(CH$_3$)$_2$], 0.78 (dd, J(HH) = 7.1 Hz, J(P,H) = 15.0 Hz, 6H, CH(CH$_3$)$_2$]. − ^{13}C NMR (50.3 MHz, [D_6]benzene): δ = 175.0 [J(Pt,C) = 1170 Hz, CO], 149.3, 148.0, 144.3, 143.1, 139.8, 139.0, 135.3, 133.9 (8 m, C_6F_5), 25.8 [J(P,C) = 27 Hz, J(Pt,C) = 26 Hz, CH(CH$_3$)$_2$], 18.9 [J(Pt,C) = 16 Hz, CH(CH$_3$)$_2$]. − ^{31}P NMR (81 MHz, [D_6]benzene): δ = 36.6 [s, J(Pt,P) = 2124 Hz].

$C_{22}H_{21}F_{10}OPPt$ (717.45) Calcd. C 36.83 H 2.95
  Found C 37.09 H 3.17

[Bis(pentafluorophenyl)(triisopropylphosphine)platinum]bis-(methylcyclopentadienyl){μ-[(1,2,3-η:5-η)-5-oxo-2-pentene-1,5-diyl-O]}zirconium (6b): This compound was obtained as described for complex **4b**: Starting from 0.25 g (0.82 mmol) of **1b** and 0.60 g (0.83 mmol) of **5**, 0.62 g of a yellow solid was obtained (**6b**, 74% yield); m.p. 142 °C (dec.). − ^{1}H NMR (200 MHz, [D_8]tetrahydrofuran): δ = 6.02, 5.87, 5.79, 5.66 (4 m, 8H, $CH_3C_5H_4$), 4.89 (m, 1 H, 3-H), 4.32 (dd, 2H, 4-H, -H′), 2.11, 2.06 (2 s, 6H, CH_3C$_5$H$_4$), 1.39 [dd, 3 H, J(H,H) = 7.2 Hz, J(Pt,H) = 14.1 Hz, CH(CHᵃ₃)(CH^{b}₃)], 1.19 [dd, 3H, J(H,H) = 7.2 Hz, J(P,H) = 13.3 Hz, CH(CHᵃ₃)-(CH^{b}₃)]. − ^{13}C NMR (50.3 MHz, [D_8]tetrahydrofuran): δ = 311.1 (CO[22]), 149.0, 144.8, 139.7, 136.2 (4 m, C_6F_5), 135.1 (C-2), 120.3, 119.8 [2 s, $CH_3C(CH)_4$], 115.0, 112.2, 111.6, 110.5, 108.7, 108.2 [6 s, $CH_3C(CH)_4$], 107.5 (C-3), 65.2 [J(Pt,C) = 130 Hz, C-4], 49.8 (C-1), 26.4 [J(P,C) = 27 Hz, J(Pt,C) = 26 Hz, CH(CH)$_3$)$_2$], 20.4 [J(Pt,C) = 17 Hz, CH(CᵃH$_3$)(C^{b}H$_3$)], 19.4 [J(Pt,C) = 15 Hz, CH(CᵃH$_3$)(C^{b}H$_3$)], 14.9, 14.8 [$CH_3C(CH)_4$]. − ^{31}P NMR (81 MHz, [D_8]tetrahydrofuran): δ = 33.9 [J(Pt,P) = 2704 Hz].

$C_{38}H_{41}F_{10}OPPtZr$ (1021.00) Calcd. C 44.70 H 4.04
  Found C 45.02 H 4.38

CAS Registry Numbers

s-cis-**1a**: 83780-95-4 / *s-trans*-**1a**: 83780-93-2 / *s-cis*-**1b**: 101518-70-1 / *s-trans*-**1b**: 126574-53-6 / **3**: 97877-56-0 / *cis*-**4a**: 126329-21-3 / *trans*-**4a**: 126453-03-0 / *cis*-**4b**: 126329-22-4 / *trans*-**4b**: 126453-04-1 / **5**: 126329-23-5 / **6b**: 126329-24-6

[1] Review: G. Erker, *Angew. Chem.* **101** (1989) 411, *Angew. Chem. Int. Ed. Engl.* **28** (1989) 397.
[2] E. O. Fischer, A. Masböl, *Chem. Ber.* **100** (1967) 2445; review: K. H. Dötz, H. Fischer, P. Hofmann, F. R. Kreissl, U. Schubert,

K. Weiss, *Transition Metal Carbene Complexes*, Verlag Chemie, Weinheim 1983.
[3] F. R. Hartley in *Comprehensive Organometallic Chemistry*, (G. Wilkinson, F. G. A. Stone, E. W. Abel, Eds.), vol. 6, p. 502, Pergamon Press, Oxford 1982.
[4] E. O. Fischer, F. R. Kreissl, E. Winkler, C. G. Kreiter, *Chem. Ber.* **105** (1972) 588.
[5] A number of carbene complexes of nickel(0) of varying stabilities have been synthesized by addition reactions of Ni(CO)$_4$: W. Petz, *J. Organomet. Chem.* **90** (1975) 223; *ibid.* **72** (1974) 369; *ibid.* **55** (1973) C42; R. Lecht, *Dissertation*, University of Würzburg, 1987.
[6] J. P. Collman, L. S. Hegedus, J. R. Norton, R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed., p. 762, University Science Books, Mill Valley 1987, see, however: J. L. Simunic, A. R. Pinhas, *Organometallics* **6** (1987) 1358.
[7] E. P. Kündig, D. McIntosh, M. Moskovits, G. A. Ozin, *J. Am. Chem. Soc.* **95** (1973) 7234.
[8] D. B. Dell'Amico, F. Calderazzo, C. A. Veracini, N. Zandonà, *Inorg. Chem.* **23** (1984) 3030; S. K. Janikowski, L. J. Radonovich, T. J. Groshens, K. J. Klabunde, *Organometallics* **4** (1985) 396; T. J. Groshens, K. J. Klabunde, *J. Organomet. Chem.* **259** (1983) 337.
[9] R. J. Angelici, *Acc. Chem. Res.* **5** (1972) 335; T. Yoshida, Y. Ueda, S. Otsuka, *J. Am. Chem. Soc.* **100** (1978) 3941; J. E. Byrd, J. Halpern, *ibid.* **93** (1971) 1634; J. Cherwinski, H. C. Clark, *Inorg. Chem.* **10** (1971) 2263; H. C. Clark, W. J. Jacobs, *ibid.* **9** (1970) 1229; H. C. Clark, K. R. Dixon, W. J. Jacobs, *J. Am. Chem. Soc.* **91** (1969) 1346; *J. Chem. Soc. D*, **1968**, 548.
[10] In fact, the reaction of *cis*-PtCl$_2$(CO)$_2$ with a secondary amine has been suggested to proceed via an unstable dialkylamino(hydroxy)carbene intermediate, which is deprotonated by an excess of NHR$_2$ to give the isolable carboxamido complex; see: D. B. Dell'Amico, F. Calderazzo, G. Pellizi, *Inorg. Chem.* **18** (1979) 1165.
[11] This behavior has also been observed for some neutral platinum complexes: R. F. Heck, *Palladium Reagents in Organic Synthesis*, p. 341, Academic Press, London 1985; H. C. Clark, K. von Werner, *Synth. React. Inorg. Met. Org. Chem.* **4** (1974) 355; M. Hidai, K. Kokura, Y. Uchida, *J. Organomet. Chem.* **52** (1973) 431.
[12] P. Giannoccaro, A. Sacco, G. Vasapollo, *Inorg. Chim. Acta* **37** (1979) L455.
[13] R. Usón, J. Forniés, M. Tomás, B. Menjón, *Organometallics* **4** (1985) 1912.
[14] G. Erker, C. Krüger, G. Müller, *Adv. Organomet. Chem.* **24** (1985) 1.
[15] In those cases where the formation of a metal oxycarbene complex originating from a group-4 (η^4-butadiene)metallocene complex and a metal carbonyl is reversible, the use of the hafnium reagent is advisable to favor the carbene complex formation: G. Erker, R. Lecht, R. Schlund, K. Angermund, C. Krüger, *Angew. Chem.* **99** (1987) 708; *Angew. Chem. Int. Ed. Engl.* **26** (1987) 666.
[16] P. Chini, G. Longoni, *J. Chem. Soc. A*, **1970** 1542.
[17] G. Erker, R. Lecht, J. L. Petersen, H. Bönnemann, *Organometallics* **6** (1987) 1962.
[18] G. Erker, U. Dorf, R. Benn, R.-D. Reinhardt, J. L. Petersen, *J. Am. Chem. Soc.* **106** (1984) 7649; see also ref.[1].
[19] Complex **3** is known to easily undergo substitution of one carbonyl group by a wide variety of monodentate ligands (see ref.[20]).
[20] R. Usón, J. Forniés, M. Thomás, B. Menjón, *Organometallics* **5** (1986) 1581.
[21] B. Heyn, B. Hipler, G. Kreisel, H. Schreer, D. Walther, *Anorganische Synthesechemie*, p. 76, Springer, Berlin 1986.
[22] Complexity of the signals precluded the determination of J(Pt,C).

[13/90]