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Preliminary communication

The synthesis and reactivity of N-bonded η^1-1-azaallyl type complexes of platinum(II) and palladium(II). Crystal structure of $[Pt\{CH{=}C(NHCOMe)C(O)O\}(PMe_2Ph)_2]$

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Abstract

Reaction of *cis*-$[MCl_2L_2]$ (M = Pt, L = PPh_3, $PMePh_2$, PMe_2Ph, $PBzPh_2$, $L_2 = Ph_2PCH_2PPh_2$ {dppm}, $Ph_2P\{CH_2\}_2PPh_2$, $Ph_2P\{CH_2\}_3PPh_2$ or $Ph_2P\{CH_2\}_4PPh_2$; M = Pd, $L_2 = Ph_2P\{CH_2\}_3PPh_2$) with α-acetamidocinnamic acid and silver(I) oxide affords quantitative yields of the N-bonded η^1-1-azaallyl complexes $[M\{N(COMe)C({=}CHPh)C(O)O\}L_2]$; in contrast, the analogous reaction of *cis*-$[MCl_2L_2]$ (L = PPh_3, $PMePh_2$, PMe_2Ph; $L_2 = Ph_2P\{CH_2\}_4PPh_2$) with 2-acetamidoacrylic acid leads to the isolation of the metallaoxacyclopentenone products $[M\{CH{=}C(NHCOMe)C(O)O\}L_2]$, characterised by an X-ray study on the platinum complex where L = PMe_2Ph. The complex $[Pt\{N(COMe)C({=}CHPh)C(O)O\}(dppm)]$ exhibits a temperature-dependent ^1H NMR spectrum.

Although some η^3-1-azaallyl complexes have been described [1], little is known about the chemistry of the η^1-1-azaallyl system [2]. Herein we now describe the synthesis of the first examples of N-bonded η^1-1-azaallyl complexes of transition metals, some of which undergo a novel 1,3-isomerisation.

Treatment of *cis*-$[PtCl_2L_2]$ with α-acetamidocinnamic acid, **1a**, in the presence of an excess of silver(I) oxide in refluxing dichloromethane afforded quantitative yields of the air-stable complexes **2**. Similarly, complex **3a** was prepared using $[PtCl_2(dppm)]$ with 2-acetamidoacrylic acid, **1b**, and silver(I) oxide. The elemental analysis, IR and NMR spectra of complexes **2** and **3a** indicated the formation of five-membered metallacycles containing an N-bonded η^1-1-azaallyl fragment [*].

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[*] Selected spectroscopic data (coupling constants in Hz). Compound **2a**, IR (KBr disc): ν(C=O) 1650 and 1600 cm^{-1}; NMR ($CDCl_3$): ^1H (300 MHz) δ 8.29–6.87 (m, 36H, Ph + =CH) and 1.53 (s, 3H, Me); $^{13}C\{^1H\}$ (75.5 MHz) δ 176.72 (d, CO, $^3J(PC)$ 3], 172.55 (s, CO) and 21.97 (s, Me); $^{31}P\{^1H\}$ (36.2 MHz) δ 10.18 [d, PPh_3, $^1J(PtP)$ 3198, $^2J(PP)$ 24] and 5.95 ppm [d, PPh_3, $^1J(PtP)$ 4063, $^2J(PP)$ 24]. Compound **3a**, IR (KBr disc): ν(C=O) 1660 and 1590 cm^{-1}; NMR ($CDCl_3$): ^1H (300 MHz) δ 7.83–7.29 (m, 20H, Ph), 5.76 (d, 1H, $=CH_2$, $^5J(PH)$ 2], 4.71 (s, 1H, $=CH_2$), 4.34 [dd, 2H, CH_2, dppm, $^2J(PH)$ 9, 11], 2.10 (s, 3H, Me); $^{13}C\{^1H\}$ (75.5 MHz) δ 179.03 [d, CO, $^3J(PC)$ 3], 172.93 (s, CO), 144.60 (s, $>C{=}CH_2$), 105.35 (s, $>C{=}CH_2$), 47.91 [dd, CH_2, dppm, $^1J(PC)$ 32, 32], 21.90 [d, Me, $^4J(PC)$ 2]; $^{31}P\{^1H\}$ (36.2 MHz) δ −56.11 [d, dppm, $^1J(PtP)$ 2714, $^2J(PP)$ 71] and −66.47 ppm [d, dppm, $^1J(PtP)$ 3472, $^2J(PP)$ 71].

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In contrast, treatment of *cis*-$[PtCl_2L_2]$ (L = PPh_3 or $L_2 = Ph_2P\{CH_2\}_4PPh_2$) with 2-acetamidoacrylic acid, **1b**, and silver(I) oxide in refluxing dichloromethane afforded the metal–carbon bonded ring complexes **4a** and **4d**, respectively, there being no indication of the formation of N-bonded η^1-1-azaallyl systems. Interestingly, treatment of the complexes *cis*-$[PtCl_2L_2]$ (L = $PMePh_2$ or PMe_2Ph) with **1b** and silver(I) oxide led initially to the formation of the N-bonded η^1-1-azaallyl complexes **3b** and **3c**, as evidenced by their $^{31}P\{^1H\}$ NMR spectra. However, on attempted isolation, only high yields of the isomeric metal–carbon bonded ring complexes **4b** and **4c** were obtained.

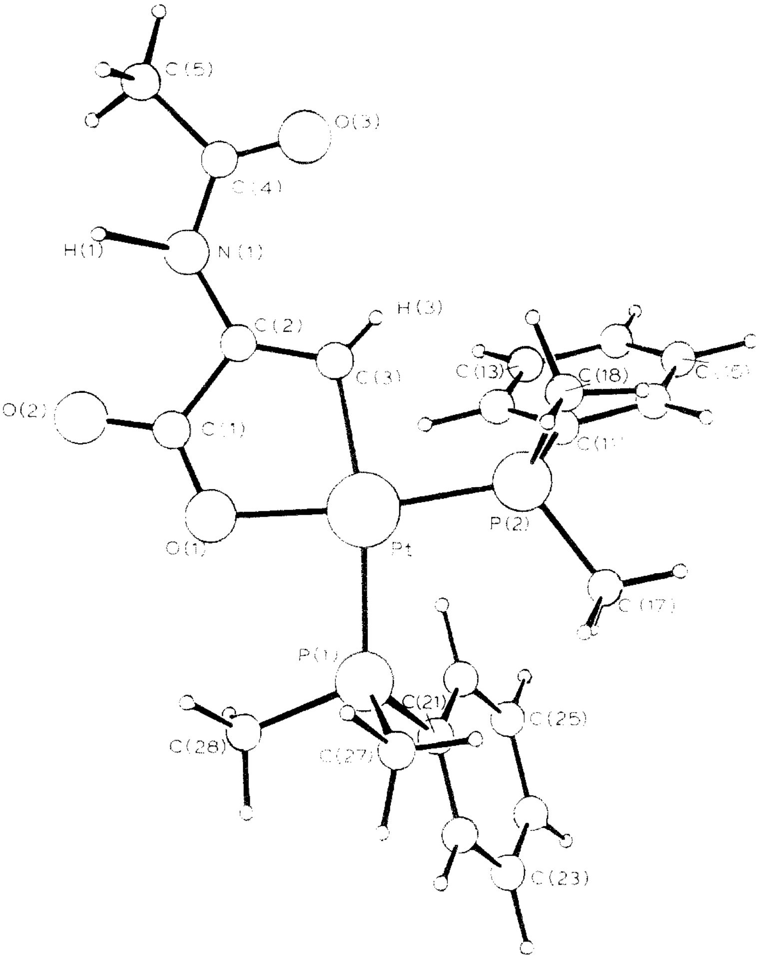
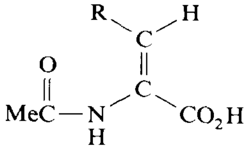
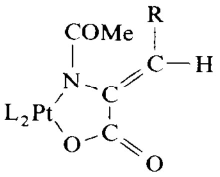


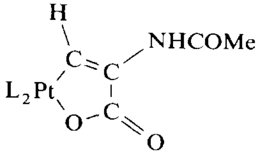
Fig. 1. Molecular structure of $[\overline{Pt\{CH{=}C(NHCOMe)C(O)O}\}(PMe_2Ph)_2]$, **4c**. Interatomic distances: Pt–P(1) 2.316(3), Pt–P(2) 2.207(2), Pt–O(1) 2.086(6), Pt–C(3) 2.027(11), C(2)–C(3) 1.331(13), C(1)–C(2) 1.498(14), C(1)–O(1) 1.267(11), C(1)–O(2) 1.244(10), C(2)–N(1) 1.420(12), N(1)–C(4) 1.346(15), C(4)–C(5) 1.498(15), C(4)–O(3) 1.233(13) Å. Angles: P(1)–Pt–P(2) 100.2(1), P(1)–Pt–O(1) 87.0(2), P(2)–Pt–C(3) 90.6(3), C(3)–Pt–O(1) 82.2(3), Pt–C(3)–C(2) 110.5(8), Pt–O(1)–C(1) 111.8(6), O(1)–C(1)–C(2) 117.0(8), C(1)–C(2)–C(3) 118.3(9)°.



(**1 a**; R = Ph;
b; R = H)



(**2** R = Ph, **a**, L = PPh$_3$;
b, L = PMePh;
c; L = PMe$_2$Ph;
d, L = PBzPh$_2$;
e; L$_2$ = dppm;
f; L$_2$ = Ph$_2$P(CH$_2$)$_2$PPh$_2$;
g; L$_2$ = Ph$_2$P(CH$_2$)$_3$PPh$_2$;
h; L$_2$ = Ph$_2$P(CH$_2$)$_4$PPh$_2$)
(**3** R = H, **a**; L$_2$ = dppm
b; L = PMePh$_2$
c; L = PMe$_2$Ph)



(**4 a**, L = PPh$_3$;
b, L = PMePh$_2$;
c, L = PMe$_2$Ph;
d; L$_2$ = Ph$_2$P(CH$_2$)$_4$PPh$_2$)

The molecular structure **4c** has been confirmed by a single-crystal X-ray structure determination *. The molecular geometry is illustrated in Fig. 1. The complex contains a five-membered platinaoxacyclopentenone ring system, the coordination about the platinum atom is essentially square planar and the Pt–C(3)–C(2)–C(1)–O(1) ring is also effectively planar. The non-hydrogen atoms of the nitrogen-bonded side chain deviate only slightly from the plane of the ring, and are oriented such that atoms C(1)–C(2)–N(1)–C(4)–C(5) lie in a W conformation. The appropriate bond

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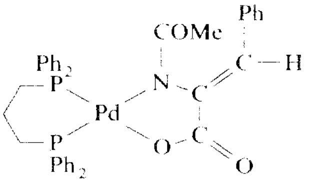
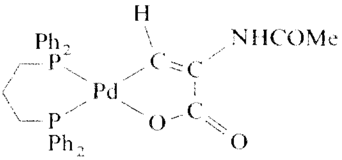
* *Crystal data:* Crystals of **4c** were grown slowly from dichloromethane–light petroleum in air. Data were collected at 293 K using Mo-K_α X-radiation, $\lambda = 0.7107$ Å, on a Stöe STADI-2 Weissenberg diffractometer. The unit cell parameters were determined by least-squares refinement of omega measurements for different layers. $C_{21}H_{27}NO_3P_2Pt$, $M = 599.4$, 0.17×0.30×0.50 mm, monoclinic, space group $I2/c$ (non-standard $C2/c$), $a = 15.546(1)$, $b = 10.982(1)$, $c = 27.274(1)$ Å, $\beta = 109.3(1)°$, $U = 4394.7$ Å^3, $Z = 8$, $D_c = 1.81$ g cm^{-3}, λ(Mo-K_α) = 62.78 cm^{-1}; final R 0.0395 (R_w 0.0396). Intensities of 3084 reflections in the range $7 < 2\theta < 54°$ were measured. The data were corrected for Lorentz and polarisation effects to give 2733 independent reflections with [$I > 3\sigma(I)$]. An absorption correction was applied to the data with the maximum and minimum transmission factors 0.4821 and 0.3277, respectively. Phenyl rings were included as rigid groups with D_{6h} symmetry and C–C distances of 1.395 Å. The hydrogen atoms of the phenyl and methyl groups were included in calculated positions (C–H 1.08 Å) and had fixed isotropic thermal parameters. Other hydrogen atoms were located by difference Fourier and refined as free variables. Table of atom coordinates and a complete list of bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre.

distances and angles in **4c**, as expected, compare well to the corresponding lengths and angles in $[\mathrm{Pt}\{\overline{\mathrm{CH{=}CHC(O)O}}\}(\mathrm{PPh_3})_2]$ [3].

The formation of the carbon-bonded ring system present in the complexes **4** presumably proceeds via formation of the respective N-bonded η^1-1-azaallyl system followed by isomerisation to a C-bonded azaallyl complex and a 1,3-hydrogen shift. The isolation of the N-bonded isomer **3a** when L = dppm and the C-bonded isomers **4a** or **4d** when L = PPh_3 or $Ph_2P(CH_2)_4PPh_2$ clearly shows that the isomerisation is ligand dependent. As with the reactions of *cis*-$[PtCl_2L_2]$ (L = $PMePh_2$ or PMe_2Ph), both isomers can be detected in the reactions of either $[PtCl_2L_2]$ (L_2 = $Ph_2P\{CH_2\}_2PPh_2$ or $Ph_2P\{CH_2\}_3PPh_2$) with silver(I) oxide and 2-acetamidoacrylic acid, **1b**. It is also interesting to note that no related isomerisation is observed with the phenyl-substituted N-bonded η^1-1-azaallyl systems **2**. Similar results were obtained with palladium(II); treatment of $[PdCl_2(Ph_2P\{CH_2\}_3PPh_2)]$ with silver(I) oxide and **1a** afforded the N-bonded η^1-1-azaallyl complex **5**, whereas analogous treatment of the same metal complex with **1b** gave the metal–carbon bonded product **6**.



(**5**)



(**6**)

Complex **2e** exhibits a temperature-dependent ^{1}H NMR spectrum, the dppm methylene protons appearing as a very broad signal at 25 °C and as a sharp doublet of doublets with platinum-195 satellites at +90 °C *. This temperature dependence appears to be associated with the presence of the cinnamyl and phosphine phenyl groups which force the acetamido group out of a planar arrangement [4]. Thus, at −30 °C the dppm methylene protons can be seen to be inequivalent, and appear as an ABXX′ spin system. In contrast, the dppm methylene protons of complex **3a** are equivalent at room temperature and appear as a doublet of doublets in its ^{1}H NMR spectrum. Some evidence for an acetyl–phenyl interaction in **2e** is provided by the observation that the methyl protons of the acetyl group in this complex are more shielded than those in **3a**. In addition, preliminary X-ray data for the benzyldiphenylphosphine complex **2d** show that the acetyl group is not coplanar with the five-membered ring.

Acknowledgements. We thank the SERC for financial support, Johnson Matthey plc for the generous loan of platinum metal salts, Dr R.S. Atkinson for helpful discussions and Ms A. Flammer for help with the X-ray crystal structure determination.

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* Selected ^{1}H NMR data (300 MHz, coupling constants in Hz) for the dppm methylene protons of compound **2e**, +25 °C ($CDCl_3$), δ 4.38 (m, br, 2H, CH_2, dppm); +90 °C (DMSO-d_6) δ 4.42 [dd, 2H, CH_2, dppm, ^2J(PH) 11, 11, ^3J(PtH) 62]; −30 °C ($CDCl_3$), δ 4.82 [ddd, 1H, CH_2, dppm, ^2J(PH) 10, 10, ^2J(HH) 16] and 4.07 ppm [ddd, 1H, CH_2, ^2J(PH) 12, 12, ^2J(HH) 16].

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Erratum

Re: Methyl–iodine exchange in (η^5-iodocyclopentadienyl)metallo methyl derivatives of iron(II), tungsten(II), and molybdenum(II) in the presence of palladium; by C. Lo Sterzo (J. Organomet. Chem., 408 (1991) 253–259)

On page 258, first heading: compound **7** should be (η^5-$CH_3C_5H_4$)$W(CO)_3I$; second heading: compound **8** should be (η^5-$CH_3C_5H_4$)$Mo(CO)_3I$.