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SIDE-BONDED KETONE COMPLEXES OF PLATINUM(0). ALLOXAN AND DIETHYL OXOMALONATE COMPLEXES AND REACTIONS OF PLATINUM(0) COMPLEXES WITH ISATIN AND BENZOYL CYANIDE.

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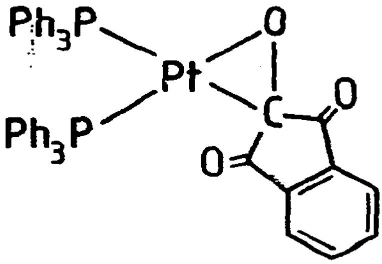
Summary

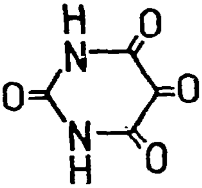
Reactions of alloxan (all) with [PtL($PPh_3)_2$] (L'= trans-stilbene, L" diphenylacetylene) afford the side-bonded ketone complex [Pt(all)($PPh_3)_2$] which may also be obtained from the hydrate of alloxan and [PtL'($PPh_3)_2$]. Similarly diethyl oxomalonate (dio) and [Pt($PPh_3)_4$] afford a side-bonded ketone complex [Pt(dio)($PPh_3)_2$]. Reaction of isatin with [Pt($PPh_3)_4$] gives trans-[PtH{$\overline{\mathrm{NCO}(o\text{-}C_6H_4)\mathrm{CO}}$}($PPh_3)_2$] and benzoyl cyanide and [PtL'($PPh_3)_2$] give cis-[Pt(CN)(COPh)($PPh_3)_2$] and trans-[Pt($CN)_2$($PPh_3)_2$].

Introduction

The polyvicinal ketone, indan -1,2,3-trione, contains an electron deficient carbonyl group[1] and can displace triphenylphosphine, trans-stilbene and diphenylacetylene from the zerovalent platinum complexes [Pt($PPh_3)_4$], [Pt(trans-PhCH=CHPh)($PPh_3)_2$], or [Pt(PhC≡CPh)($PPh_3)_2$] to give the side-bonded trione compound (1).[2] This observation prompted



(1)



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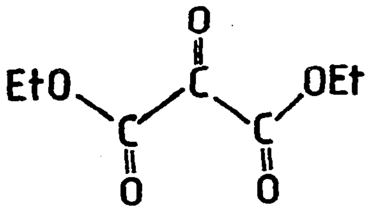

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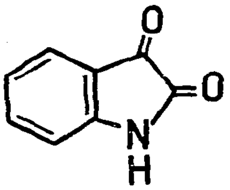
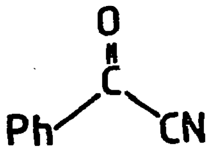


(4)

us to investigate the behaviour of the electrophilic ketones, alloxan (2) and diethyl oxomalonate (3), together with isatin (4), and benzoyl cyanide (5) towards zerovalent platinum compounds.

Results and Discussion

Treatment of a benzene solution of trans-stilbenebis(triphenylphosphine)platinum(0) with an equimolar quantity of alloxan(2) gave a complex Pt(alloxan)$(PPh_3)_2$ (6). The physical properties of (6) support



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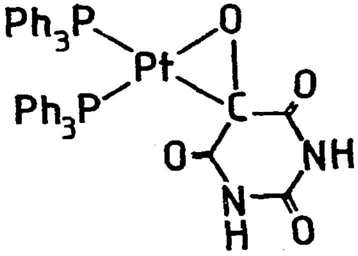


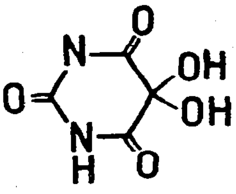
(6)

a structure in which the central carbonyl group of the trione is co-ordinated to platinum via its pπ-pπ orbitals in a similar fashion to (1). Thus the formation of (6) would be consistent with the ability of the central carbonyl group of alloxan to act as a dienophile in Diels-Alder reactions.[3] Furthermore, the i.r. spectrum of (6) exhibits medium to strong carbonyl absorptions at 1716, 1694, 1682 and 1648 cm^{-1}, similar to those observed in Diels-Alder adducts of alloxan.[3]

Alloxan is also able to displace diphenylacetylene from $[Pt(PPhC{\equiv}CPh)(PPh_3)_2]$ to give (6) and this side-bonded alloxan complex may also be obtained by reaction of the hydrate of alloxan (7) with [Pt(<u>trans</u>-$PhCH{=}CHPh)(PPh_3)_2]$. This ability of zerovalent platinum to displace water from (7) is analogous to the formation of (1) via the hydrate of indan-1,2,3-trione.[1]

Alloxanbis(triphenylphosphine)platinum(0) reacts with both dioxygen and hexafluoropropanone to give white and yellow solids respectively. However, pure samples of these products could not be obtained and they showed very broad absorptions in the ν(C=O) regions of their i.r. spectra. The reactions of dioxygen and hexafluoropropanone with (1) have been shown to lead to cyclic-dicarboxylate and ring-expansion products respectively.[1]

The reaction between tetrakis(triphenylphosphine)platinum(0) and diethyl oxomalonate (3) produces the white air-stable complex (8). The i.r. spectrum of (8) shows a C=O frequency associated with the CO_2Et groups at 1680 cm^{-1}. The free ketone (3) exhibits a band at 1770 cm^{-1} due to the ketonic carbonyl[4] and the absence of this band in the complex (8) is consistent with its formulation as a side-bonded ketone complex. Furthermore just as the central carbonyl group of the cyclic triones (1) and (2) has been shown to act as the dienophile in room-temperature Diels-Alder reactions with buta-1,3-diene and 2-methyl buta-1,3-diene



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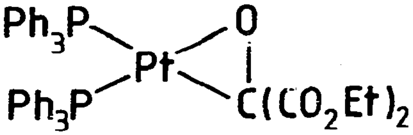
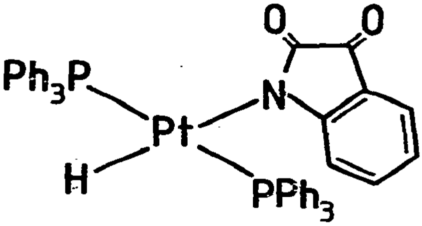


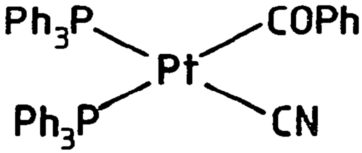
(8)

diethyl oxomalonate reacts similarly with dienes at elevated temperature.[1] The diethyl oxomalonate in (8) is displaced by 1,3-dichlorotetrafluoropropan-2-one to give the oxidative-addition product cis-[$PtCl(CF_2COCF_2Cl)(PPh_3)_2$].[5] The reactions of methyl- and ethyl oxalyl chloride, $ClCOCO_2R$, (R = Me or Et) with [$Pt(PPh_3)_4$] at room temperature have been shown to lead to the oxidative-addition products [$PtCl(COCO_2R)(PPh_3)_2$].[6]

Neither [$Pt(PPh_3)_4$] nor [Pt(trans-PhCH=CHPh)($PPh_3)_2$] react with isatin (4), at room temperature and no side-bonded ketone complex is formed with this non-electrophilic ketone. However, treatment of [$Pt(PPh_3)_4$] with isatin (4), in refluxing benzene affords dark-red crystals of stoichiometry [Pt(isatin)($PPh_3)_2$] (9). The i.r. spectrum of (9) shows no N-H stretching frequency but exhibits a band at 2175 cm^{-1} in the region of ν(Pt-H) and C=O stretching frequencies at 1723 and 1674 cm^{-1}. The ^1H n.m.r. spectrum of (9) shows a triplet resonance on the high field side of tetramethylsilane at 21.8τ [$J(^{31}P-^1H)$ 14.5Hz] characteristic of a platinum-hydride resonance coupling to two equivalent ^{31}P nuclei thus defining a trans configuration for (9). As a result of



(9)



(10)

the limited solubility of the complex the satellite signals due to $^{195}Pt-^{1}H$ coupling were not observed. These data indicate that oxidative-addition of the N-H bond of isatin to platinum(0) has occurred to give a hydrido-complex. Similar hydrido-complexes of platinum(II) have been prepared by the reaction of imides with zerovalent platinum complexes.[7] The absence of a strong i.r. band in the 540-560 cm^{-1} region of the i.r. spectrum of (9) is in agreement with its trans-configuration.[8]

Trifluoroacetyl cyanide (CF_3COCN) is known to react with Vaska type compounds of iridium(I) and rhodium(I) to give side-bonded carbonyl compounds.[9] Since indan-1,2,3-trione forms a side-bonded ketone complex with $[Pt(PPh_3)_2]$ but not with trans-$[IrCl(CO)(PPh_3)_2]$[2] it seemed possible that PhCOCN might co-ordinate to the more nucleophilic $Pt(PPh_3)_2$ via its $p\pi$-$p\pi$ C=O orbitals. However, treatment of trans-stilbenebis (triphenylphosphine)platinum(0) with PhCOCN at room temperature gives (10). The i.r. spectrum of (10) shows C≡N and C=O stretches at 2144 and 1629 cm^{-1} respectively compared with ν(C≡N) at 2225 and ν(C=O) at 1680 cm^{-1} for free PhCOCN. The strong ν(C=O) band of (10) appears in the region for metal acyl C=O absorptions[10] suggesting that CO-CN carbon-carbon bond cleavage has occurred. Furthermore a strong band at 543 cm^{-1} is indicative of a cis-arrangement of triphenylphosphine ligands.[8] The oxidative-addition of cyanogen to $[Pt(PPh_3)_4]$ has also been shown to involve cis-addition of the substrate to platinum(0) to give cis-$[Pt(CN)_2(PPh_3)_2]$.[11] The cleavage of C-CN bonds has also been observed in studies on the reactions of $MeC(CN)_3$ with $[Pt(PPh_3)_4]$ [12] and PhCN with various zerovalent compounds of nickel, palladium, and platinum.[13-16] Cleavage of the C-CN bond in PhCN may proceed via an intermediate side-bonded nitrile complex and such a complex $[Ni(\eta^2\text{-}N{\equiv}CPh)(PPh_3)_2]$,[17] analogous to $[Pt(\eta^2\text{-}N{\equiv}CCF_3)(PPh_3)_2]$ [18] and $[Mo(\eta^2\text{-}N{\equiv}CR)(C_5H_5)_2]$, (R = Me, CF_3, or Ph),[19] has been reported. The oxidative-addition of PhCOCN to platinum(0) may occur via an intermediate side-bonded carbonyl complex and the isolation of the cis-complex (10) would be consistent with this type of mechanism. Both of the compounds $[\mathrm{Pt}\{(\mathrm{NC})_2\mathrm{C{=}C(CN)}_2\}(\mathrm{PPh}_3)_2]$ and $[\mathrm{Pt(NCC{\equiv}CCN)(PPh}_3)_2]$ are known to isomerise to $[\mathrm{Pt(CN)}\{\mathrm{C(CN){=}C(CN)}_2\}(\mathrm{PPh}_3)_2]$ and *cis*-$[\mathrm{Pt(CN)}\{\mathrm{C{\equiv}C(CN)}\}(\mathrm{PPh}_3)_2]$ respectively upon photolysis.[20,21]

In addition to (10) a white crystalline solid characterised as *trans*-$[\mathrm{Pt(CN)}_2(\mathrm{PPh}_3)_2]$ can also be isolated from the reaction of PhCOCN with $[\mathrm{Pt}($*trans*-$\mathrm{PhCH{=}CHPh)(PPh}_3)_2]$.

The studies described in this paper indicate that ketones such as (1), (2) and (3), which are sufficiently electrophilic to form hydrates, also have the ability to form side-bonded ketone compounds with platinum(0). However, isatin and benzoyl cyanide do not form hydrates, and side-bonded ketone compounds have not been isolated with these ketones.

Experimental

^{1}H n.m.r. spectra were recorded on a JEOL PS100 spectrometer. Infrared spectra were obtained as Nujol and hexachlorobutadiene mulls on a Perkin-Elmer 225 spectrophotometer between KBr(4000-400 cm^{-1}) and polythene (400-200 cm^{-1}) plates. Molecular-weight determinations were carried out by Beller Mikroanalytisches Laboratorium and microanalyses by Pascher Mikroanalytisches Laboratorium and the Butterworth Microanalytical Consultancy Limited.

The compounds $[\mathrm{Pt(PPh}_3)_4]$,[22] $[\mathrm{Pt}($*trans*-$\mathrm{PhCH{=}CHPh)(PPh}_3)_2]$,[23] and $[\mathrm{Pt(PhC{\equiv}CPh)(PPh}_3)_2]$ [24] were prepared as described in the literature. Alloxan was prepared from its hydrate by heating at 150°C under *vacuo*. All reactions were carried out under a dry oxygen-free nitrogen atmosphere, with solvents dried and distilled under nitrogen before use. Light petroleum refers to the fraction having b.p. 30-40°C.

Reactions of alloxan. - Alloxan (0.16g, 1.1 mmol) and trans-stilbenebis-(triphenylphosphine)platinum(0) (1g, 1.1 mmol) were stirred together in benzene (150 cm^3) for 3d. The resulting buff-coloured solid was filtered and the residue was rapidly recrystallised from dichloromethane-diethyl ether as buff crystals of (6) (0.7g, 73%). (Found: C,55.8; H,3.7; N,3.1; 0,7.2; M,1088, $CHCl_3$. $C_{40}H_{32}N_2O_4P_2Pt$ requires C,55.8; H,3.7; N,3.3; 0,7.4%; M,861.8); ν_{max} at 3160m, and 3047m (N-H), 1739w,sh, 1716s, 1694m, 1682m,sh and 1648s, (C=0), 1581vw, 1567vw, 1480m, 1476m,sh, 1441m, 1433s, 1730s, 1312vw, 1252m, 1231m, 1184vw, 1156w, 1105m, 1094m, 1070vw, 1038vw, 1025vw, 867w, 844w, 805w, 776w, 771w,sh, 767m, 760w,sh, 754w,sh, 747m, 722vw, 712m, 699s, 647vw, 624vw, 558w,sh, 547m, 531s, 522s, 511m, 503s cm^{-1}.

Similarly, diphenylacetylenebis(triphenylphosphine)platinum(0) (0.5g, 0.56 mmol) and alloxan (0.08g, 0.56mmol) gave (6) (0.4g, 83%).

Reaction of alloxan hydrate with trans-stilbene bis(triphenylphosphene) platinum(0). - Alloxan hydrate (0.09g, 0.56 mmol) and trans-stilbenebis (triphenylphosphine)platinum(0) (0.5g, 0.56 mmol) were stirred together in benzene (75 cm^3) for 3d. The resulting buff-coloured solid was filtered and rapidly recrystallised from dichloromethane-diethyl ether to give (6) (0.3g, 66%) identified by comparison of its i.r. spectrum with an authentic sample.

Reaction of diethyl oxomalonate with tetrakis(triphenylphosphine) platinum(0). - An excess of diethyl oxomalonate (0.5 cm^3) was added with stirring to a suspension of tetrakis(triphenylphosphine)platinum(0) (1.0g, 0.69 mmol) in diethyl ether (30 cm^3). After stirring at room temperature for 24h the white precipitate was filtered and the residue was washed with diethyl ether and dried in vacuo to give (8) (0.6g, 89%) m.p. 159-161°C. (Found: C,57.2; H,4.5; 0,8.9. $C_{43}H_{40}O_5P_2Pt$ requires C,57.7; H,4.5; 0,8.5%); ν_{max} at 1680s,br, (C=0), 1582w, 1568w, 1358s, 1258s, 1240s, 1178s, 1149s, 1088s, 1050s, 1025m, 996m, 980m, 920w, 876m, 855m, 810w, 758s, 746s, 738s, 700s, 692s, 630m, 622m, 544s, 522s, 512s, 495s, 453m, and 420w, cm^{-1}. The ^{1}H n.m.r. spectrum in $CDCl_3$ solution showed resonances at τ 2.68 (m, 30H, C_6H_5), 6.06 (m, 4H, $\underline{CH_2}CH_3$), and 8.96[t, 6H, $CH_2\underline{CH_3}$, J (HH) 6.6Hz].

1,3-dichlorotetrafluoropropan-2-one (0.5 cm^3) and (8) (0.3g, 0.34 mmol) in diethyl ether, (30 cm^3) were stirred for 24h at room temperature to give white *microcrystals* of *cis*-$[PtCl(CF_2COCF_2Cl)(PPh_3)_2]$ (0.23g, 75%), m.p. 230°C. Lit. value 230-234°C,[5] and identified by comparison of its i.r. and ^{19}F n.m.r. spectra with that of an authentic sample.[5]

Reaction of isatin with tetrakis(triphenylphosphine)platinum(0). - Isatin (0.06g, 0.41 mmol) and tetrakis(triphenylphosphine)platinum(0) were refluxed in benzene (50 cm^3) for 12h. The red solution was rotary evaporated under reduced pressure to 10 cm^3 and on standing dark-red *crystals* of (9) were deposited which were filtered, washed with diethyl ether and dried *in vacuo*. (0.3g, 86%), m.p. 218-220°C. (Found: C,60.6; H,4.0; N,1.8; M,834,$CHCl_3$. $C_{44}H_{35}NO_2P_2Pt$ requires C,61.0; H,4.1; N,1.6; M,866); ν_{max} at 2175m, (Pt-H), 1723s, and 1674s, (C=O), 1608s, 1596m,sh, 1583s, 1565vw, 1480m, 1462s, 1326m, 1307m, 1296w, 1269w, 1221m, 1188w,sh, 1182w, 1156w, 1142w, 1095s, 1026w, 973vw, 917w, 868vw, 840m, 824w, 760s, 748m, 743m, 729vw, 717s, 699s, 673vw, 624w, 552vw, 528s, 524s,sh, 516m,sh, 509m, 488vw, and 477w, cm^{-1}. The ^{1}H n.m.r. spectrum in $CDCl_3$ solution showed resonances at τ 2.6(m,34H, C_6H_5, C_6H_4) and 21.8τ [t,1H,PtH,J(PH) 14Hz, J(PtH) not discernable].

Reaction of benzoyl cyanide with trans-stilbenebis(triphenylphosphine) platinum(0). - Benzoyl cyanide (0.15g, 1.1mmol) and *trans*-stilbenebis-(triphenylphosphine)platinum(0) (1g, 1.1 mmol) were stirred together in benzene (30 cm^3) for 12h at room temperature. The orange solution was reduced in volume (to 10 cm^3) by evaporation under reduced pressure and addition of diethyl ether and a small amount of light petroleum gave a pale-yellow solid. Recrystallisation of the filtered solid from dichloromethane light petroleum gave pale yellow _prisms_ of (10)(0.3g, 32%), m.p. 187-189°C. (Found; C,61.8; H,4.3; N,1.7. $C_{44}H_{35}NOP_2Pt$ requires C,62.2; H,4.2; N,1.7%); ν_{max} at 2144w, (C≡N), 1629s, (C=O), 1590w, 1576w, 1569w. 1478s, 1437s,sh, 1432s, 1301vw, 1184m, 1156m, 1096s, 1070vw, 1024vw, 976vw, 883s, 774w, 762m, 750m, 744m, 710s, 697s, 692s,sh, 681w, 648s, 625vw, 620vw, 543s, 528s, 520s, 514m, and 503m, cm^{-1}.

The filtrate was treated with activated charcoal at room temperature and filtered and the solvent was removed _in vacuo_. The white residue was dissolved in dichloromethane and addition of diethyl ether followed by slow evaporation under reduced pressure gave a white solid. Recrystallisation from dichloromethane-benzene-diethyl ether gave white _crystals_ of _trans_-[$Pt(CN)_2(PPh_3)_2$] (0.15g, 35%) m.p. 330°C (decomp.), (lit.[25] > 325°C, decomp.) ν(C≡N) at 2135 cm^{-1} (lit.[25] 2130 cm^{-1}); ν_{max} at 2135m, (C≡N) 1584vw, 1568vw, 1480m, 1339s, 1334s,sh, 1330w, 1306w, 1182w, 1155w, 1098s, 1095m,sh, 1067vw, 1024w, 755s, 717m, 700s, 684vw, 622vw, 530s, 518s, 511m, and 489w, cm^{-1}.

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