Carbonylchloro[2-(phenylazo)phenyl-*C,N*]platinum and Cyclopentadienyl[2-(phenylazo)phenyl-*C,N*]platinum

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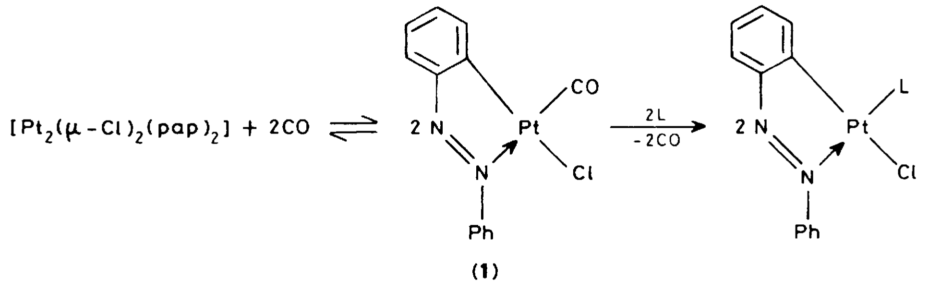
The 2-(phenylazo)phenyl complex $[Pt_2(\mu\text{-}Cl)_2(pap)_2]$ is much less reactive than its palladium analogue. Whilst CO cleaves the chloride bridges to afford [PtCl(pap)(CO)], this readily loses CO to reform the starting material. Treatment of [PtCl(pap)(CO)] with other ligands displaced CO, but failed to initiate any insertions of CO into the Pt–C bond. Treatment of $[Pt_2(\mu\text{-}Cl)_2(pap)_2]$ with $Tl(C_5H_5)$ caused no reaction, but [PtCl(pap)(CO)] reacted smoothly with $Tl(C_5H_5)$ to produce $[Pt(C_5H_5)(pap)]$.

Cyclopentadienyl[2-(phenylazo)phenyl-*C,N*]-nickel and -palladium have been known for many years. The former is readily made from the reaction of azobenzene and nickelocene, $[Ni(C_5H_5)_2]$,[1] whereas the latter compound is best synthesized from the reaction of di-μ-chloro-bis[2-(phenylazo)phenyl-*C,N*]dipalladium, $[Pd_2(\mu\text{-}Cl)_2(pap)_2]$, with cyclopentadienylthallium.[2] The platinum analogue of these complexes has not previously been described, however, and several attempts to synthesize it in our laboratories by the reaction of $[Pt_2(\mu\text{-}Cl)_2(pap)_2]$ and cyclopentadienylthallium in various solvents met with failure, no change resulting, even with a ten-fold excess of $Tl(C_5H_5)$. We have now developed a synthetic route to $[Pt(C_5H_5)(pap)]$, involving initial cleavage of the chloride bridges of $[Pt_2(\mu\text{-}Cl)_2(pap)_2]$ by a weak ligand, prior to replacing the chlorides by cyclopentadienyl. Such bridge-cleavage reactions are well documented for strong ligands such as tertiary phosphines.[3,4]

Results and Discussion

The reaction of carbon monoxide with $[Pt_2(\mu\text{-}Cl)_2(pap)_2]$ readily produced a single isomer of the carbonyl derivative, (1), isolated as orange crystals [equation (1)]. Though compound (1) has been mentioned previously in the patent literature,[5] no details were described. On standing or heating, it readily loses CO, in the solid phase or in solution, reforming the chloride bridges. The value of 298 cm^{-1} for ν(Pt–Cl) is similar to those of analogues with PR_3 *trans* to nitrogen,[4] suggesting that the geometry of compound (1) is as shown. The value of ν(CO), 2 118 cm^{-1}, is less diagnostic. The CO of (1) was readily displaced by treatment with a variety of stronger or less volatile ligands in solution [equation (1), L = PEt_3, $PMePh_2$, $AsPh_3$, or NH_2Bu^i]. Even dropwise addition of dilute solutions of the ligands failed to promote any carbonyl insertion, contrary to what has been found with some other platinum carbonyl compounds.[6,7]

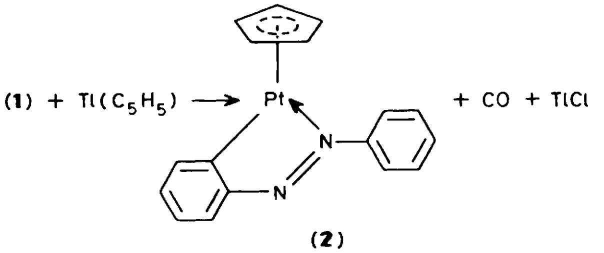


(1)

(1)

Solutions of compound (1) on treatment with $Tl(C_5H_5)$ immediately react to form deep red solutions of $[Pt(C_5H_5)(pap)]$, (2) [equation (2)], which can be isolated as red-black crystals indefinitely stable in air. The ^1H n.m.r. spectrum in $CDCl_3$ exhibits a cyclopentadienyl signal at δ 5.85 p.p.m., ^2J(PtH) 17 Hz, consistent with the expected η^5 bonding.[8] Clearly compound (2) resists attack by CO in solution.

We have no explanation for the failure of $[Pt_2(\mu\text{-}Cl)_2(pap)_2]$ to react with $Tl(C_5H_5)$. Steric hindrance is unlikely to apply, as the palladium reaction proceeds readily,[2] and $Tl(C_5H_5)$ reacts readily with some other chloride-bridged platinum complexes.[8] The ease of reforming $[Pt_2(\mu\text{-}Cl)_2(pap)_2]$ from (1) by CO elimination may, however, indicate that the chloride bridges are particularly strong in that compound. Eliminations of weak ligands resulting in the formation of halide bridges are well known,[9] but for CO loss usually the stronger-bonding iodide is necessary. We observed a slow loss of NH_2Bu^i from solid $[PtCl(pap)(NH_2Bu^i)]$, and this, too, would be in keeping with such an explanation. The limit seems to be at arsenic or phosphorus donors. No decomposition by ligand loss occurred with [PtCl(pap)L] (L = $AsPh_3$ or PEt_3) in solution for several hours, or from the solid over 10 years.



(2)

(2)

Experimental

N.m.r. spectra were recorded on a Perkin-Elmer R.32 instrument, and i.r. spectra on a Perkin-Elmer 577 spectrometer. The compound $[Pt_2(\mu\text{-}Cl)_2(pap)_2]$ was prepared by the published method.[3]

Carbonylchloro[2-(*phenylazo*)*phenyl*-C,N]*platinum*, (**1**).—Carbon monoxide was bubbled through a solution of $[Pt_2(\mu\text{-}Cl)_2(pap)_2]$ (98 mg, 1.2 mmol) in benzene (100 cm^3) for 4 h, during which time the colour changed from maroon to orange. Vacuum removal of the benzene left the product as an orange powder (101 mg, 98%). Recrystallization was achieved by adding hexane, saturated with CO, to the benzene solution, and maintaining a CO atmosphere. M.p. 116—136 °C (decomp.) (Found: C, 35.8; H, 2.2; N, 6.4. $C_{13}H_9ClN_2OPt$ requires C, 35.5; H, 2.1; N, 6.4%).

Chloro[2-(*phenylazo*)*phenyl*-C,N](*triphenylarsine*)-*platinum*.—A solution of compound (**1**) was prepared *in situ* by bubbling CO through a suspension of $[Pt_2(\mu\text{-}Cl)_2(pap)_2]$ (10 mg, 0.012 mmol) in benzene (5 cm^3). The solution was cooled to 10 °C and a solution of $AsPh_3$ (8.5 mg, 0.027 mmol) in benzene (2.5 cm^3) was added dropwise. The orange colour was replaced by maroon. I.r. monitoring showed the disappearance of the band at 2 118 cm^{-1}, and no band in the acyl region. Solvent was removed under vacuum and the *product* recrystallized from ethanol as maroon crystals, 14.5 mg (84%), m.p. 245—247 °C (Found: C, 49.6; H, 3.6; N, 4.1. $C_{30}H_{24}AsClN_2Pt$ requires C, 50.2; H, 3.4; N, 3.9%).

Reactions of compound (**1**) with PEt_3, $PMePh_2$, and NH_2Bu^i were similarly performed and yielded the known compounds $[PtCl(pap)(PEt_3)]$,[4] $[PtCl(pap)(PMePh_2)]$,[4] and $[PtCl(pap)(NH_2Bu^i)]$,[3] respectively.

Cyclopentadienyl[2-(*phenylazo*)*phenyl*-C,N]*platinum* (**2**).—A solution of compound (**1**) was prepared *in situ* by bubbling CO through a suspension of $[Pt_2(\mu\text{-}Cl)_2(pap)_2]$ (0.8 g, 0.96 mmol) in diethyl ether (150 cm^3) for 3 h. Finely ground $Tl(C_5H_5)$ (2.4 g, 9.1 mmol) was added and the mixture was stirred for 30 min, whilst maintaining a slow stream of CO through the reaction vessel. The orange colour was replaced by deep red. Filtration removed the TlCl and excess of $Tl(C_5H_5)$ (1.31 g), and removal of the solvent left the product as a sticky black solid (0.95 g). Recrystallization from light petroleum (b.p. 40—60 °C) and ether produced the pure product as red-black crystals, 0.37 g (43%), m.p. 104—105 °C (Found: C, 46.2; H, 2.6; N, 6.2. $C_{17}H_{14}N_2Pt$ requires C, 46.3; H, 3.2; N, 6.35%).

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