Convenient Synthesis of Diacyl Complexes of Platinum(II) via Novel Stereoselective CO Insertion and Acyl Scrambling of Trans Acyl Alkyl Complexes of Platinum. A Mechanistic Model of Palladium-Catalyzed Coupling and Carbonylative Coupling of Acid Halides with Organometals

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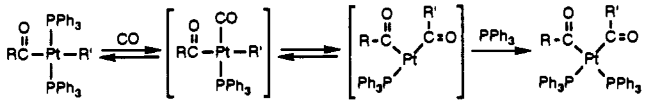
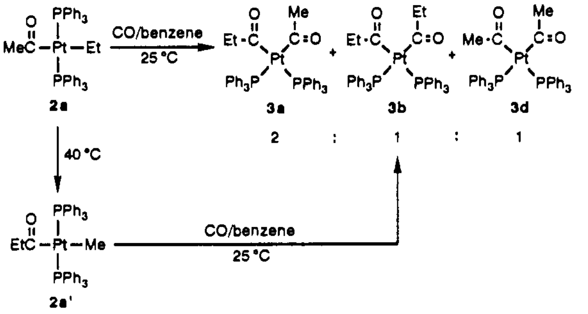
The palladium-catalyzed coupling reactions of acid chlorides with organometal reagents are useful for the synthesis of ketones.[1] Mechanistic studies suggest that the acyl alkyl complex of Pd(II), presumably resulting from transmetalation between the acylhalopalladium and organotin species, serves as a crucial intermediate in these reactions. However, no detection of such complexes or their platinum analogues has been achieved.[2] Tanaka reported the carbonylative coupling between diorganozincs and acid halides to yield α-diketones and proposed a mechanism involving a intermediacy of diacyl complexes but without direct evidence.[3] Described herein are the convenient synthesis of trans acyl alkyl complexes of platinum(II) and the unique carbonylation reactions of such complexes including one with intriguing acyl scrambling, exclusively leading to the *cis*-diacyl products and finally to the diketones and ketones. It is proposed that these results provide the first good model for the Pd-catalyzed coupling and carbonylative coupling of acid halides with organometals.

Treatment of *trans*-$Pt(COR)(X)(PPh_3)_2$ (R = Me, X = Br (**1a**); R = Et, X = Cl (**1b**); R = Ph, X = Cl (**1c**))[4] with ZnR'_2 (R′ = Et, Ph) in benzene at 25 °C resulted in the formation of *trans*-$Pt(COR)(R')(PPh_3)_2$ (R = Me, R′ = Et (**2a**); R = R′ = Et (**2b**); R = Ph, R′ = Et (**2c**); R = Et, R′ = Ph (**2c′**)) in high yields.[5] It had been previously believed that complexes containing ligands of high trans-influence at trans disposition would be unstable, and therefore they have escaped attention.[6] To our knowledge, these are the first well-characterized examples of d^8 square planar acyl alkyl complexes of trans geometry.[7]

Scheme I



Scheme II



In the presence of CO at 25 °C, complex **2b** readily underwent stereoselective carbonylation to yield *cis*-$Pt(COEt)_2(PPh_3)_2$ (**3b**) exclusively. In a similar fashion, both complexes **2c** and **2c′** were transformed to *cis*-$Pt(COPh)(COEt)(PPh_3)_2$ (**3c**).[8] Such transformations afford a convenient synthetic route to the novel *cis*-diacyl complexes of Pt(II). The reactions of **2b** and **2c** were complete on mixing the reactants judging from immediate NMR measurements. Since the analogous reaction of the phenyl complex **2c′** was substantially slower than those of the ethyl derivatives, alkyl (or aryl) migration is likely a critical step of these carbonylation processes. Rapid displacement of PPh_3 in **2b** by $P(OPh)_3$ suggests that the mechanism is probably preceded by the substitution of CO for a PPh_3. The following migratary CO insertion consequently resides the cis disposition of the two acyl ligands as shown in Scheme I.[6c,9] An alternative mechanism comprising the association of CO with the complex to give a five-coordinate intermediate followed by the carbonylation and isomerization certainly can not be excluded.

At 40 °C, *trans*-$Pt(COMe)(Et)(PPh_3)_2$ (**2a**) was transformed to *trans*-$Pt(COEt)(Me)(PPh_3)_2$ (**2a′**) in 80% yield. Complex **2a′** did not revert to **2a**, and no similar reaction has been observed for other acyl alkyl analogues. Bubbling CO through the solution of **2a** or **2a′** for less than 10 min afforded the expected *cis*-$Pt(COEt)(COMe)(PPh_3)_2$ (**3a**), but surprisingly also the *cis*-dipropionyl and -diacetyl complexes (**3b** and **3d**) in a ratio 2:1:1 (Scheme II). The deliberate addition of **3b** to a product mixture from which over 90% of **3d** had been removed did not show any change in the relative abundance of the three diacyl derivatives even after 30 h at 25 °C. This evidence excludes the possibility that such novel intermolecular "acyl scrambling" arises from the dis-

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(5) Treatment of 300 mg of *trans*-$Pt(COPh)(Cl)(PPh_3)_2$ with 0.24 mL of $ZnEt_2$ (1 M in *n*-hexane solution) in 10 mL of N_2-degassed benzene at 25 °C for 45 min resulted in the formation of **2c**. Addition of *n*-hexane caused the precipitation of **2c**. Recrystallization from benzene/*n*-hexane gave a yellow product in 82% yield. Selected spectral data: IR (KBr) $\nu_{CO} = 1560\ cm^{-1}$; ^{31}P NMR ($CDCl_3$) δ 25.43 ($J_{P-Pt} = 3395$ Hz); ^1H NMR ($CDCl_3$) δ 0.13 (t, 3 H, $J_{H-H} = 7.7$ Hz, $J_{H-Pt} = 27.0$ Hz, CH_3 (Et)), 0.36 (q, 2 H, $J_{H-H} = 7.7$ Hz, $J_{H-P} = 7.4$ Hz, $J_{H-Pt} = 47.0$ Hz, CH_2 (Et)). Anal. Calcd for $C_{45}H_{40}OP_2Pt$: C, 63.30; H, 4.72. Found: C, 62.86; H, 4.72.

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(8) Bubbling CO through a benzene solution containing 50 mg of **2b** under atmospheric pressure at 25 °C for 20 min led to the formation of **3b** exclusively. The addition of hexane to the solution resulted in the crystallization of the product in 98% yield. Selected spectral data: IR (KBr) $\nu_{CO} = 1635, 1611\ cm^{-1}$; ^{31}P NMR (C_6D_6) δ 14.01 ($J_{P-Pt} = 1540$ Hz); ^1H NMR (C_6D_6) δ 0.78 (t, 6 H, $J_{H-H} = 7.2$ Hz, CH_3), 2.55 (q, 4 H, $J_{H-H} = 7.2$ Hz, CH_2).

(9) The reaction of **2b** and $P(OPh)_3$ resulted in instantaneous formation of $Pt(COEt)(Et)(PPh_3)(P(OPh)_3)$ in which PPh_3 and $P(OPh)_3$ are at trans positions, in good yield.

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proportionation of **3a**, **3b**, or **3d**. A possible mechanism is that the carbonylation of **2a** or **2a′** involves an intermediate with bridging acyl ligands. Alkylation of bridging carbonyls to form η^2-acyl moieties, and interconversions between vicinal and geminal bis(η^2-acyl) ligands in di- or trinuclear complexes have been recognized.[10] Detailed mechanistic studies are in progress.

Heating **2c′** in benzene at 40 °C for 3.5 h resulted in the decomposition of 20% of the complex, yielding PhC(O)Et. In contrast, **2c** showed no change under similar conditions. Recalling the irreversible isomerization of **2a** to **2a′**, one would conclude that the facility for decarbonylation of the acyl group must be important to the stability of *trans*-Pt(COR)(R′)(PPh_3)$_2$.[11] Thermal decomposition of **3c** in benzene at 50 °C led to the formation of PhC(O)Et and PhC(O)C(O)Et in a ratio of 2:1 in 90% total yield. These results strongly suggest that acyl alkyl complexes and diacyl complexes play the key roles in the reactions of catalytic coupling and carbonylative coupling of acid halides with organometals respectively.

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Supplementary Material Available: Text giving experimental procedures and spectral data for all complexes (4 pages). Ordering information is given on any current masthead page.

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