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PREPARATION OF NEW Pt- AND Ni-CONTAINING CYCLIC ESTERS AND THEIR REACTIVITIES

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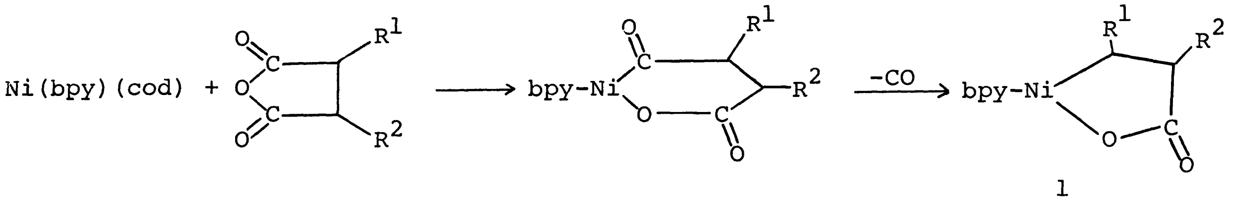
New Pt- or Ni-containing cyclic esters ($\text{PCy}_3\overline{\text{PtCOCH}_2\text{CH}_2\text{COO}}$, $(\text{PCy}_3)_2\overline{\text{PtCOCH}_2\text{CH}_2\text{COO}}$, dpe-$\overline{\text{PtCOCH}_2\text{CH}_2\text{COO}}$, dpe-$\overline{\text{NiCH}_2\text{CH}_2\text{COO}}$, and bpy-$\overline{\text{NiCH}_2\text{CH}_2\text{CH}_2\text{COO}}$; PCy_3 = tricyclohexylphosphine, dpe = 1,2-bis-(diphenylphosphino)ethane, bpy = 2,2'-bipyridine) are prepared by oxidative addition of the corresponding cyclic carboxylic anhydrides to Pt(0) or Ni(0) complexes.

Previously we reported the preparation of transition metal-containing cyclic esters by the reactions of the corresponding zero-valent transition metal complexes with α,β- or β,γ-unsaturated acid.1) Uhlig and his coworkers reported the preparation of similar Ni-containing 5-membered cyclic esters by an independent reaction route, an oxidative addition of cyclic carboxylic anhydrides to Ni(bpy)(cod) (cod = 1,5-cyclooctadiene) followed by decarbonylation from an intermediate 6-membered 2-oxo-nickelacyclic esters.2) However, characterization of their complexes is based only on elemental analysis and position of ν(C=O) bands in IR spectra of the complexes, and more detailed examination of structures of the complexes by other instrumental analyses and chemical reactivities of the complexes is necessary for unequivocal characterization of the complexes.



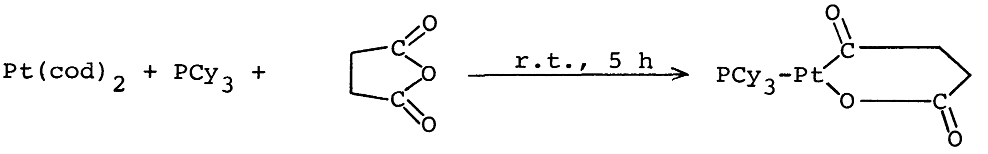
(1)

1

In order to develop the chemistry of the transition metal-containing cyclic ester type complexes, we have expanded the reaction (1) by using other transition metal complexes as well as other cyclic carboxylic anhydrides. Oxidative additions of acyclic carboxylic anhydrides to Ni(0) and Pd(0) complexes have been already reported.3)

Pt-Complexes.

A reaction of $\text{Pt(cod)}_2$4) with a mixture of PCy_3 (1 mol/Pt(cod)_2) and succinic anhydride (1 mol/Pt(cod)_2) in THF at room temperature afforded a white insoluble complex, which is considered to have the following platinacyclic structure as judged from its IR (ν(C=O): 1560vs, 1650m) and analytical data (Found: C, 46.3; H, 6.7. Calcd.: C, 45.9; H, 6.4). When 2 mol of $\mathrm{PCy_3}$ per mol of $\mathrm{Pt(cod)_2}$ was added,

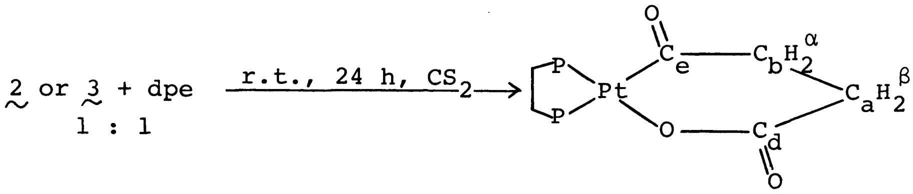


1 : 1 : 1

2 (yield = 34%)

(2)

the reaction afforded a similar platinacyclic complex 3 having two $\mathrm{PCy_3}$ ligands, $(\mathrm{PCy_3})_2\overline{\mathrm{PtCOCH_2CH_2COO}}$, in 37% yield. 3: Anal. Found: C, 56.1; H, 8.2. Calcd.: C, 56.2; H, 8.7. IR: 1610vs, 1640sh (ν(C=O)). Low solubility of these complexes prevented analyzing their structures by NMR spectroscopy. However, a ligand exchange reaction with dpe in $\mathrm{CS_2}$ gave a soluble dpe-coordinated complex, 4. By



4 (yield = ca. 45%)

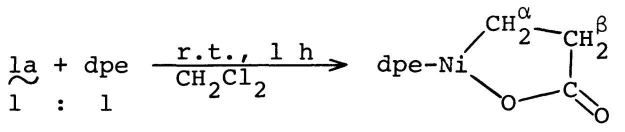
(3)

using dpe-d_4 ($\mathrm{Ph_2PCD_2CD_2PPh_2}$), we prepared 4-$d_4$. 4: Anal. Found: C, 52.0; H, 4.5. Calcd.: C, 51.9; H, 4.4. IR: 1630vs (ν(C=O)). ^{1}H-NMR ($\mathrm{CD_2Cl_2}$, r.t.) of 4-d_4: δ: 2.2 (2H, td, ^3J(H-H) = 6.1 Hz, ^4J(P-H) = 2.4 Hz, H^α), 2.9 (2H, t, ^3J(H-H) = 6.1 Hz, H^β), 7.5-7.9 (20H, m, Ph). ^{13}C{^{1}H}-NMR ($\mathrm{CD_2Cl_2}$, r.t., ppm from TMS): 36.0-42.7 (m, $\underline{\mathrm{C}}\mathrm{H_2}$ of dpe), 46.6 (t, ^4J(C-P) = 8,45 Hz, $\mathrm{C_a}$), 50.95 (d, ^3J(C-P) = 36.62 Hz, $\mathrm{C_b}$), 127.1-134.0 (m, Ph), 205.6 (d, ^3J(C-P) = 3.7 Hz, $\mathrm{C_d}$), 240.3 (s, $\mathrm{C_e}$). ^{31}P{^{1}H}-NMR ($\mathrm{CD_2Cl_2}$, r.t., ppm from external $\mathrm{PPh_3}$): 38.3 (d, ^2J(P-P) = 4.4 Hz) with satellites (^1J(P-Pt) = 1430.2 Hz), 43.5 (d, ^2J(P-P) = 4.4 Hz) with satellites (^1J(P-Pt) = 3510.9 Hz).

The appearance of H^α and $\mathrm{C_b}$ signals at relatively low magnetic fields in the ^{1}H- and ^{13}C{^{1}H}-NMR spectra, respectively, supports the non-decarbonylated 2-oxo-platinacyclic ester structure of 4 shown above. Complexes 2-4 are the first examples of Pt-containing cyclic esters. The 2-oxo-platinacyclic ester complexes, 2-4, are less susceptible to the decarbonylation reaction in contrast to occurrence of the facile decarbonylation reaction of their nickel analogues (Eq (1)). Complexes 2-4 have considerably high stability against air.

Ni-Complexes.

Analogously to the report by Uhlig[2)] the bpy-coordinated Ni complex 1a ($\mathrm{R^1 = R^2 = H}$) was obtained by the reaction of Ni(bpy)(cod) with succinic anhydride,[5)] but low solubility and low stability of 1a in solvents prevented obtaining a reasonably good NMR spectrum. The bpy complex 1a was, as in the case of the Pt complexes, converted into a soluble and stable dpe complex by a ligand exchange reaction,

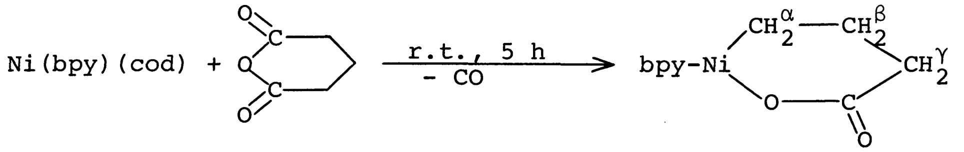


5 (yield = 33%) (4)

In our previous works we observed that Ni-containing cyclic ester type complexes having the dpe ligand had high stability and solubility in solvents,[1)] and dpe had a much higher coordinating ability toward di-valent organonickel complexes.[6)] From good ^{1}H-, $^{13}C\{^{1}H\}$-, and $^{31}P\{^{1}H\}$-NMR spectra of the soluble and stable complex 5, we obtained unequivocal evidence that 5 had the structure shown above.

5: Anal. Found: C, 66.0; H, 5.3. Calcd.: C, 65.8; H, 5.3. IR: 1635vs (ν(C=O)). Use of dpe-d_4 gave 5-d_4. ^{1}H-NMR (CD_2Cl_2, r.t.) of 5-d_4:δ: 0.8 (2H, ddt, ^{3}J(H-P) = 8.8 Hz, ^{3}J(H-P') = 5.1 Hz, ^{3}J(H-H) = 4.7 Hz, H^{α}), 2.3 (2H, ddt, ^{4}J(H-P) = 6.6 Hz, ^{4}J(H-P') = 3.9 Hz, ^{3}J(H-H) = 4.7 Hz, H^{β}), 7.5-7.9 (20H, m, Ph). $^{13}C\{^{1}H\}$-NMR (CD_2Cl_2, r.t., ppm from TMS): 18.6 (dd, ^{2}J(C-P) = 60.1 Hz, ^{2}J(C-P') = 23.5 Hz, $\underline{C}H_2^{\alpha}$), 22.6 (dd, ^{1}J(C-P) = 29.3 Hz, ^{2}J(C-P') = 11.7 Hz, $\underline{C}H_2$ of dpe), 28.4 (dd, ^{1}J(C-P) = 30.8 Hz, ^{2}J(C-P') = 22.0 Hz, $\underline{C}H_2$ of dpe), 37.9 (s, CH_2^{β}), 190.8 (d, ^{3}J(C-P) = 6.1 Hz, CO). $^{31}P\{^{1}H\}$-NMR (CD_2Cl_2, r.t., ppm from external PPh_3): 41.2 s, 64.9 s. The appearance of the H^{α} and $\underline{C}H_2^{\alpha}$ signals at considerably high magnetic fields in the ^{1}H- and $^{13}C\{^{1}H\}$-NMR spectra, respectively, indicates the presence of the CH_2 group directly bonded to Ni. Complex 5 is air-sensitive.

When glutaric anhydride was employed in the reaction with Ni(bpy)(cod) in THF, a new six-membered ring compound, 6, was obtained.



(5)

6 (yield = 44%)

6: Anal. Found: Ni, 19.5. Calcd.: Ni, 19.5. Microanalysis of 6 was not feasible due to its high sensitivities to air. IR: 1670vs (ν(C=O)), 1360s. Complex 6 has moderate solubility in organic solvents, but its NMR signals are somewhat broadened (possibly by a paramagnetic character of 6 or contamination with paramagnetic decomposition product(s) of 6). ^{1}H-NMR (CD_2Cl_2, r.t.):δ: 0.8 (2H, br, H^{α}), 1.3 (2H, br, H^{β}), 2.2 (2H, br, H^{γ}), 7.8-9.0 (8H, m, bpy).

The reaction of 6 with CO (1 atm, excess) in CH_2Cl_2 afforded glutaric anhydride which is considered to be formed through CO-insertion and reductive elimination,

$$6 + \mathrm{CO} \xrightarrow{\text{r.t., 24 h}} \text{glutaric anhydride} \qquad \text{(yield = 29\%)} \qquad (6)$$

These observations support the structure of 6 shown above. On treatment with maleic anhydride, a typical π-acid (excess), at reflux temperature of CH_2Cl_2, 6 undergoes β-elimination reaction to release 3-butenoic acid quantitatively,

$$\mathbf{6} + \text{maleic anhydride} \xrightarrow{\text{CH}_2\text{Cl}_2\text{, reflux, 10 min}} \text{3-butenoic acid (yield = 100\%)} + \text{Ni(bpy)(maleic anhydride)}_2 \quad (7)$$

When dpe was added to a CS_2 solution of **6**, a facile ligand exchange reaction took place to give a dpe-coordinated complex. However, the six-membered ring structure was no longer maintained in the dpe-coordinated complex as reported in our previous paper,[1b] and we obtained a ring-contracted 5-membered complex, dpe-$\overline{\text{NiCH(CH}_3\text{)CH}_2\text{COO}}$,[1b] instead of a 6-membered complex.

On the contrary to the Pt(0) and Ni(0) complexes, Pd(0) complexes, $Pd(PCy_3)_2$ which has coordinative unsaturation[7] and bis(1,5-diphenyl-1,4-pentadiene-3-one)-palladium,[8] did not show any apparent change on interaction with the cyclic carboxylic anhydrides at room temperature. A coordinatively unsaturated Rh(I) complex, $RhCl(PPh_3)_3$, showed no apparent change on the interaction with the cyclic carboxylic anhydrides, either.

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