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Preliminary communication

1,8-Diazabicyclo[5.4.0]undec-7-ene as a ligand in an intermediate in selective carbonyl substitution of a ruthenium-cobalt complex

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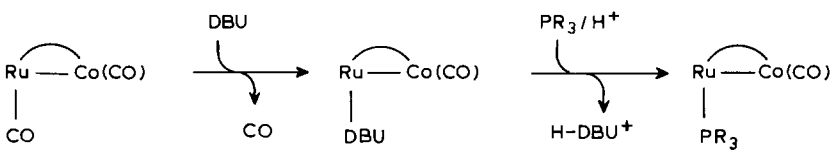
Abstract

1,8-Diazabicyclo[5.4.0]undec-7-ene, DBU, reacts with $(OC)_4Ru(\mu\text{-}PPh_2)Co(CO)_3$ (**1**) at room temperature to give an intermediate **2**, which on protonation in the presence of CO regenerates **1** and on protonation in the presence of PMe_3 gives the monosubstituted product $(OC)_3(L)Ru(\mu\text{-}PPh_2)Co(CO)_3$ (**3** L = PMe_3). DBU promotes the selective formation of **4** (L = PPh_2Me) or **5** (L = $Ph_2PCH_2C(Me)=CH_2$) in one-step from **1**, Ph_2PH, and methyl iodide or methallyl chloride, respectively.

Thermally- or photochemically-promoted carbonyl substitution reactions of mononuclear or polynuclear carbonyl complexes by phosphines usually do not lead selectively to monosubstituted or disubstituted compounds. More selective and general methods of carbonyl substitutions have been found recently [1], such as: (i) the catalytic addition of a nucleophile or an anion to the carbonyl ligand of clusters [2,3]; (ii) oxidation of the carbonyl ligand into the weakly-bonded carbon dioxide ligand by trimethylamine oxide [4–6]; and (iii) the catalysed one-electron transfer reduction [7] or oxidation [8] of metal carbonyls. We now report a new method based on the use of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) which selectively displaces one carbonyl ligand at the ruthenium site of the Ru–Co complex $(OC)_4Ru(\mu\text{-}PPh_2)Co(CO)_3$ (**1**) [9], and can be selectively substituted by phosphorus ligands in the presence of acid, as depicted in eq. 1.



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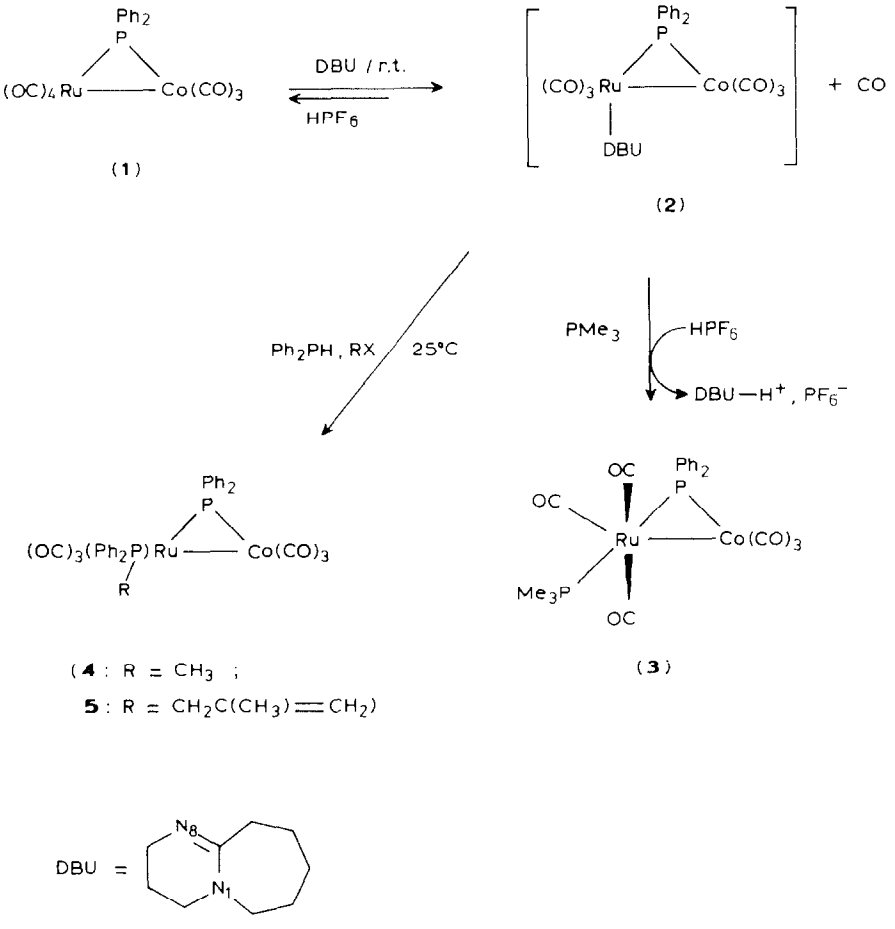

Scheme 1.

In thermal carbonyl substitution reactions of the heterobimetallic complex $(OC)_4Ru(\mu\text{-}PPh_2)Co(CO)_3$ (**1**) by phosphines substitution took place only at the Ru site but without selectivity between mono- and di-substitution [10]. An attempt to achieve to carbonyl substitution of **1** by the Ph_2P^- anion, generated from Ph_2PH and the strong organic base DBU, revealed that DBU itself selectively displaced one carbonyl ligand at the ruthenium atom.

The red complex **1** was treated at room temperature in THF with a slight excess of DBU; this immediately gave an unstable orange intermediate which could not be isolated but was identified as **2** (Scheme 1) on the basis of the experiments described below.

The ^1H NMR (CD_2Cl_2) signals of free DBU (δ 1.5–3.3 ppm) are not present in the spectrum of **2** but there are corresponding signals at δ 0.9–3.3 ppm. ^{31}P NMR (CD_2Cl_2, 193 K) spectroscopic studies showed that the (μ-PPh_2) singlet at δ 187.3 ppm for **1** was shifted to δ 198.5 ppm for **2**. This new low field singlet was consistent with the retention of a bridging (Ph_2P) ^{31}P nucleus and the disappearance of **1**.

Protonation of a THF solution of **2** with HPF_6 led to partial decomposition and a small amount of **1** was recovered. In the presence of carbon monoxide the same

treatment gave almost quantitatively the precursor **1**. Protonation of **2** with HPF_6 in the presence of an excess of PMe_3 immediately gave a deep red complex, which was identified as **3**, the monosubstituted product at the ruthenium site (^{31}P NMR (CD_2Cl_2, 223 K, 32.38 MHz): δ (ppm) 182.4 (d, μ-PPh_2), −15.2 (d, PMe_3), ^2J(PP) 95.0 Hz) [10]. The nature of **3** suggests that DBU is coordinated to the Ru atom in **2**. Separate formation of the intermediate **2** is not required for the observation of the selective monosubstitution at the ruthenium; thus addition of DBU (0.4 mmol) to a stirred THF solution of **1** (0.2 mmol), PMe_3 (0.4 mmol) and HPF_6 (0.4 mmol) at room temperature resulted in a rapid reaction, and after 5 min stirring complex **3** was isolated in 50% yield.

Treatment of **2** with an excess of the more bulky and less basic PPh_3 phosphine and HPF_6 did not give the product of PPh_3 substitution of **1**, but instead decomposition of **2** into **1** was observed. Since it is known that carbonyl substitution of **1** by PPh_3 occurs on heating [10], this indicates that the intermediate, resulting from the elimination of DBU on protonation, undergoes either faster decomposition, or faster CO and PMe_3 fixation, than PPh_3 coordination at room temperature.

It is noteworthy that when a THF solution of **2** was treated with PMe_3 in the absence of acid no substitution reaction was observed, even on reflux. The DBU ligand is thus strongly bonded, and also inhibits further carbonyl substitution of **2** since heating of complex **1** with an excess of PMe_3 gave a quantitative yield of the disubstituted product [10].

The strong DBU-Ru bond in **2** suggests that DBU is coordinated through its (sp^2)N(8) atom rather than its (sp^3)N(1) atom, for it is well known that tertiary alkyl amines give weaker bonds with metal than do imines.

The transformation **1** → **2** → **3** has been used for selective formation of monosubstituted complexes **4** (Ph_2PMe) and **5** ($Ph_2PCH_2C(Me)=CH_2$) in one step directly from **1** and Ph_2PH. The phosphine Ph_2PH alone does not react with a THF solution of **2**, but in the presence of methyl iodide at room temperature formation of **4** was observed. When the reaction was carried out in the presence of $NaPF_6$, pure complex **4** was obtained in 79% yield; this **4** was previously obtained in 15% yield, along with 60% of the disubstituted derivative, from **1** and $PMePh_2$ at 60 °C [10]. The presence of $NaPF_6$ favors the precipitation of NaI from the organic solution, thus reducing the possibility of the coordination of the iodide, and leads to the formation of $[Ph_2P(Me)H]^+PF_6^-$, which is responsible for the protonation of the DBU ligand of **2** and the release of DBU (eq. 2)).

$$Ph_2PH + CH_3I \xrightarrow{NaPF_6} [Ph_2P(Me)H]^+PF_6^- + NaI \qquad (2)$$

A similar reaction was attempted with methallyl chloride directly from **1**. Thus 0.4 mmol of DBU was added to a THF solution of **1** (0.2 mmol) at 25 °C containing 0.4 mmol of $NaPF_6$, methallyl chloride, and Ph_2PH. After 3 min stirring, complex **5** was isolated in a 80% yield. In solution (CD_2Cl_2) complex **5** exists as an equilibrium mixture of two isomers that have the phosphine ligand in the *trans* or the *cis* position with respect to the phosphido bridge and in the Ru(μ-P)Co plane (^{31}P

NMR (CD_2Cl_2, 223 K, 32.38 MHz) δ (ppm): *trans*-**5**, 183.4 (d, μ-PPh_3), 26.9 (d, $Ph_2PC_4H_7$), ^2J(PP) 102.5 Hz; *cis*-**5**, 172.3 (s, μ-PPh_2), 34.5 (s, $Ph_2PC_4H_7$); ratio *trans*/*cis* 80/20 at 223 K. Only one isomer was observed at 300 K by ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 4.96 and 4.85 (=CH_2, ^2J(HH) 3.9 Hz), 3.53 (P–CH_2, ^2J(PH) 9.7 Hz), 1.34 (CH_3)].

The one-step transformation **1** → **5** illustrates the advantage of using Ph_2PH and an alkyl halide for direct access to monosubstituted derivatives containing functional phosphines.

The important role of DBU as a basic ligand in the oxidative coupling of an alkene with carbon dioxide at a nickel center has recently been demonstrated [11]. The selective substitution reaction described here reveals a novel aspect of DBU in transition metal chemistry.

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