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C-H Bond Activation by Ruthenium(0) Complexes. Isolation of an Active Intermediate in the Ruthenium Catalyzed Aldol and Michael Reactions

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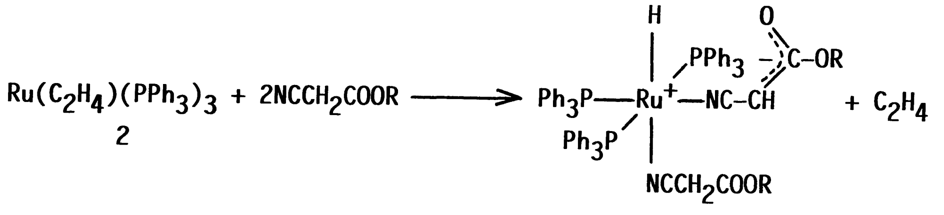
Carbon-hydrogen bond oxidative addition of alkyl cyanoacetate to $Ru(C_2H_4)(PPh_3)_3$ in benzene at room temperature gives mer-$RuH(NCCHCOOR)(NCCH_2COOR)(PPh_3)_3$ (R=Me, Et) accompanied by the liberation of ethylene. X-Ray structure analysis of the THF adduct (R=Me) reveals that NCCHCOOMe group bonds to ruthenium not through the methine carbon but the cyano group. These complexes react with benzaldehyde and methyl iodide to give alkyl (E)-1-cyanocinnamate and alkyl 2-cyanopropionate, respectively.

Carbon-hydrogen bond activation by transition metal complexes under mild conditions and their applications to organic syntheses are one of the most intriguing research subjects in organometallic chemistry. Recently Murahashi et al. reported interesting ruthenium ($RuH_2(PPh_3)_4$, **1**) catalyzed aldol and Michael reactions of active methylene compounds.[1] These reactions are of importance, since they proceed under neutral mild conditions with high chemo- and regio-selectivity. Mechanisms of these reactions are not clear at present, although they postulated a possible mechanism involving a C-H bond oxidative addition of active methylene compounds. We previously reported that $RuH_2(PPh_3)_4$ reacts with unsaturated molecules such as alkyl methacrylate to give a coordinatively unsaturated ruthenium(0) intermediate which further reacts with alkyl methacrylate giving a hydrido(alkenyl)ruthenium(II) type complex.[2] Such a C-H bond oxidative addition product is also demonstrated by the reaction of a ruthenium(0) complex $Ru(C_2H_4)(PPh_3)_3$ (**2**) with alkyl methacrylate where the initial liberation of ethylene is included.[3] We now report the isolation and structural determination of the C-H bond activation product, which is an active intermediate in the above Murahashi reaction, by the reaction of **1** or **2** with alkyl cyanoacetate.

Reaction of **2** (115.7 mg, 0.1263 mmol) with excess methyl cyanoacetate (0.639 mmol) in benzene or THF at room temperature gave a yellow solution. Ethylene (97%/Ru) was liberated during the reaction. Addition of excess hexane precipitated pale yellow crystals of the hydrido complex, mer-$RuH(NCCHCOOMe)(NCCH_2COOMe)(PPh_3)_3$ (**3**), which were purified by recrystallization from THF-hexane as a THF adduct, mer-$RuH(NCCHCOOMe)(NCCH_2COOMe)(PPh_3)_3$ 2THF (Yield 106.4 mg, 68%). A similar reaction of **2** with ethyl cyanoacetate gave **4** (Yield, 80%). Complexes **3** and **4** are thermally stable, but decompose slowly under air. These complexes were characterized mainly by IR and NMR spectroscopy and their chemical reactions.[4)]



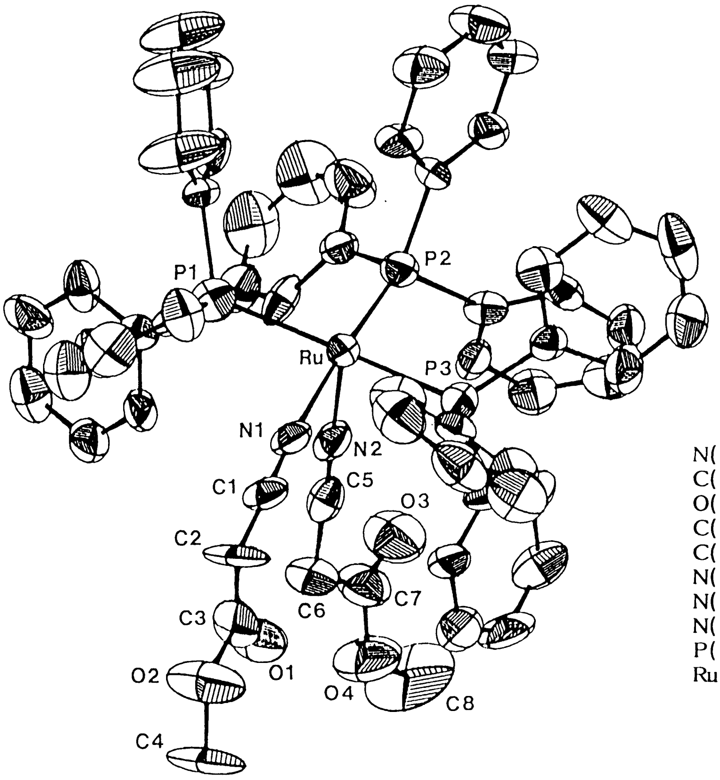
(1)

R=Me (3), Et (4)

The complexes **3** and **4** are considered to be formed by the C-H bond oxidative addition of alkyl cyanoacetate to ruthenium(0) followed by rearrangement to the linkage isomer accompanied by liberation of ethylene. It should be noted that these complexes were also obtained by the reaction of **1** with alkyl cyanoacetate. Since all of these complexes including **1**, **2**, **3**, and **4** can catalyze the Murahashi aldol type reactions of alkyl cyanoacetate with benzaldehyde as well as Michael reaction with acrylonitrile, complexes **3** and **4** are considered as active intermediates in these reactions.[5)]

Molecular structure of **3** was unequivocally determined by X-ray structure analysis.[6)] As shown in Fig. 1, **3** is essentially octahedral and the three phosphorous ligands lie in meridional configuration. The hydrido ligand is likely to occupy the site cis to P ligands where an enough room for the hydride is provided, although the hydride is not found in the differential map at present. The coordinated methyl cyanoacetate bonds to Ru through CN group which is placed on the site cis to P ligands. A noticeable feature of the structure is the bonding scheme of NCCHCOOMe group to ruthenium. Contrary to our expectation that an alkylruthenium is formed, the cyano group directly bonds to ruthenium in **3**. Dihedral angle of C(1)-C(2)-C(3)-O(1) in NCCHCOOMe group is 5.0°, indicating the planarity of these four atoms, whereas the dihedral angle for C(5)-C(6)-C(7)-O(3) in the coordinated methyl cyanoacetate is 15.8°. Slightly short C(2)-C(3) (1.38 Å) and long C(3)=O(1) (1.19 Å) bond distances are observed. The present structural feature suggests the involvement of the delocalization of π-electrons along C(2)-C(3)-O(1) bond and the considerable contribution of anionic oxo-π-allyl character for these group.[7)] Nevertheless, low molar electric conductivities of **3** and **4** in THF at room temperature (Λ=0.015 and 0.006 S cm^{2}mol^{-1}, respectively) were found, suggesting essentially their non-ionic structure.

IR spectra of **3** and **4** show two strong bands at ca. 1750 and 1600 cm^{-1} which are assignable to carbonyl stretching bands due to coordinated methyl cyanoacetate and NCCHCOOMe group, respectively. Observed low ν(C=O) value in the latter is consistent with the extensive delocalization of π-electron along the C(2)-C(3)-O(1) bond as discussed above. The hydrido stretching bands for **3** and **4** are observed at 1963 and 1950 cm^{-1}, respectively. Observation of only one ν(CN) band may be due to the accidental coincidence of ν(CN) values of coordinated methyl cyanoacetate and NCCHCOOMe group, both having a similar coordination mode.



Selected bond lengths (Å)

Ru-P(1)=2.359(5), Ru-P(2)=2.308(7),
Ru-P(3)=2.377(4), Ru-N(1)=2.10(2),
Ru-N(2)=2.15(1), N(1)-C(1)=1.12(4),
C(1)-C(2)=1.37(5), C(2)-C(3)=1.38(3),
C(3)-O(1)=1.19(3), C(3)-O(2)=1.42(6),
O(2)-C(4)=1.49(3), N(2)-C(5)=1.17(2),
C(5)-C(6)=1.45(3), C(6)-C(7)=1.51(3),
C(7)-O(3)=1.12(5), C(7)-O(4)=1.39(3),
O(4)-C(8)=1.56(3)

Selected bond angles (deg.)

N(1)-C(1)-C(2)=178(2), C(1)-C(2)-C(3)=119(3),
C(2)-C(3)-O(1)=133(4), C(2)-C(3)-O(2)=110(3),
O(1)-C(3)-O(2)=117(3), N(2)-C(5)-C(6)=173(3),
C(5)-C(6)-C(7)=107(2), C(6)-C(7)-O(3)=129(2),
C(6)-C(7)-O(4)=103(3), O(3)-C(7)-O(4)=128(2),
N(1)-Ru-N(2)=79.1(8), N(1)-Ru-P(1)=82.5(4),
N(1)-Ru-P(3)=83.1(4), N(2)-Ru-P(1)=93.0(5),
N(2)-Ru-P(2)=91.9(7), N(2)-Ru-P(3)=103.2(4),
P(1)-Ru-P(2)=97.8(2), P(2)-Ru-P(3)=99.4(2),
Ru-N(1)-C(1)=171(1), Ru-N(2)-C(5)=165(2)

Fig. 1. Molecular structure of **3** with selected bond distances and angles.

In the ^{1}H NMR spectrum of **4** at -30 °C, the hydrido proton resonates at -12.7 ppm as a quartet having couplings with three P nuclei (J=24 Hz) which are cis to the hydrido ligand. Signals assignable to methine proton appear at 2.74 ppm as a singlet, being consistent with the structural data where the NCCHCOOMe group coordinates to Ru not by the methine carbon but the CN group. At room temperature, extensive line broadening of signals due to hydrido, methine and methylene protons was observed. When free ethyl cyanoacetate is added to the C_6D_6 solution of **4**, signals due to the coordinated ethyl cyanoacetate grow and shift to high field, whereas the signals of deprotonated ethyl cyanoacetate remain intact. The result suggests the fast exchange between the coordinated ethyl cyanoacetate and free ethyl cyanoacetate in solution.

A reaction of **3** or **4** with methyl iodide gave alkyl 2-cyanopropionate in addition to alkyl cyanoacetate in good yield. The former may be formed by the electrophilic reaction of methyl iodide toward NCCHCOOMe group, whereas the latter simply by the dissociation of alkyl cyanoacetate from **3** or **4**. The resultant purple ruthenium complex is hydridoiodotris(triphenylphosphine)ruthenium(II).8) Aldol reactions of **3** and **4** with benzaldehyde also gave corresponding alkyl (E)-1-cyanocinnamates. Reaction of **4** with acrylonitrile gave the double Michael reaction product. Thus, the present results demonstrate that the isolated active intermediate in the ruthenium catalyzed aldol and Michael reactions actually does not involve any linkage between methine carbon and ruthenium, but instead the coordination of cyano group having a highly nucleophilic methine carbon is observed.

3 (or 4) + MeI Me(NC)CHCOOMe (101% for 3, 70% for 4)
+ $NCCH_2COOMe$ (85% for 3, 121% for 4) + $RuHI(PPh_3)_3$ (2)

3 (or 4) + PhCHO (E)-PhHC=C(CN)COOMe (108% for 3, 161% for 4) (3)

4 + CH_2=CHCN $(NC)(EtOOC)C(C_2H_4CN)_2$ (45%) (4)

References

1) T. Naota, H. Mizuno, and S-. I. Murahashi, J. Am. Chem. Soc., **111**, 5954 (1989).

2) S. Komiya, T. Ito, M. Cowie, A. Yamamoto, and J. A. Ibers, J. Am. Chem. Soc., **98**, 3874 (1976).

3) Although a PPh_3 ligand in **2** is orthometallated, **2** can be used as a precursor for the coordinatively unsaturated Ru(0) species: S. Komiya and A. Yamamoto, Bull. Chem. Soc. Jpn., **49**, 2553 (1976); D. J. Cole-Hamilton and G. Wilkinson, Nouv. J. Chim., **1**, 141 (1977).

4) **3**: mp 110-115 °C. IR: 2191, 1963, 1749, 1602 cm^{-1}. ^1H NMR(C_6D_6 at r t): δ -12.8 (br, 1H, RuH), 2.95 (br, 3H, CH and CH_2), 3.14 (s, 3H, OMe), 3.67 (s, 3H, OMe). **4**: mp 120-121 °C. IR: 2185, 1950, 1746, 1598 cm^{-1}. ^1H NMR (C_6D_6 at r t): δ -13.1 (br, 1H, RuH), 0.86 (t, J=7.4, 3H, Me), 1.18 (t, J=7.4, 3H, Me), 2.94 (s, 1H, CH), 3.40 (s, 2H, CH_2), 3.82 (q, J=7.4, 2H, CH_2), 4.23 (q, J=7.4, 2H, CH_2). ^1H NMR (toluene-d_8 at -30 °C): δ -12.7 (q, J=24.0, 1H, RuH), 0.87 (t, J=7.4, 3H, Me), 1.13 (t, J=7.4, 3H, Me), 2.74 (s, 1H, CH), 3.76 (s, 2H, CH_2), 3.79 (q, J=7.4, 2H, CH_2), 4.12 (q, J=7.4, 2H, CH_2).

5) **2**, **3**, and **4** (2 mol%) catalyzed aldol reactions of alkyl cyanoacetate with benzaldehyde in benzene for 17 h at rt: methyl (E)-1-cyanocinnamate, 84%(**3**); ethyl (E)-1-cyanocinnamate, 98% (**2**), 84% (**4**). Reactions of ethyl cyanoacetate with acrylonitrile catalyzed by **2** and **3** (2 mol%) for 12 h at rt gave $(NC)(EtO_2C)C(C_2H_4CN)_2$: 101% (**2**), 90% (**3**).

6) The crystal data for **3**, $RuH(NCCHCOOMe)(NCCH_2COOMe)(PPh_3)_3 \cdot 2THF$: $C_{70}H_{71}N_2O_6P_3Ru$, Fw=1230.4, triclinic, space group $P\bar{1}$, a=16.736(9) Å, b=17.291(8) Å, c=16.063(6) Å, α=92.61(4)°, β=98.74(5)°, γ=133.03(2)°, V=3286(3) $Å^3$, Z=2, d_{calcd}=1.24 g cm^{-3}, d_{obsd}=1.26 g cm^{-3} (rt), radiation Mo K_α, 0.71068 Å, 3°<2θ<40°. High angle reflection data (2θ>40°) were not collected due to their weak intensities. No. of data collected was 4661. Method of phase determination: direct method. All the non-hydrogen atoms except THF were refined anisotropically. The two solvent molecules (THF), whose occupancies were assumed to be 0.5 probably due to partial loss of THF during the measurement, and hydrogens were included in the calculation, but they were not refined. Current R values were R=0.103, R_w=0.115, S=1.54 for the observed 3991 reflections ($|F_o| > 3\sigma|F_o|$).

7) Contribution of Ru-N=C=CH-COOR canonical structure seems to be small, since the bond angle Ru-N(1)-C(1) is 171(1)° and the dihedral angle of Ru-N(1)-C(1) and C(1)-C(2)-O(1) is 7.1°. In addition ν(CN) values and CN bond lengths in the coordinated methyl cyanoacetate and the NCCHCOOMe group are quite similar, suggesting essentially their CN triple bond character.

8) $RuHI(PPh_3)_3$ was characterized spectroscopically: IR, ν(Ru-H)=2031 cm^{-1}; ^1H NMR, δ -14.6 (q, J=24.5 Hz, 1H, Ru-H). P. S. Hallman, B. R. McGarvey, and G. Wilkinson, J. Chem. Soc., A, **1968**, 3143.

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