Insertion of Electron-Deficient Olefins into the C–H Bond of 2-Furanyl- and 2-Thienylplatinum Complexes

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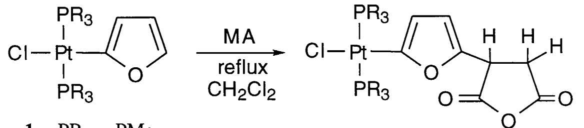
The treatment of 2-furanylplatinum with maleic anhydride (MA), tetracyanoethylene (TCNE) and 7,7,8,8-tetracyanoquinodimethane (TCNQ) results in insertion of the olefins into the C–H bond of furanyl group at the 5-position. 2-Thienylplatinum complex similarly reacts with TCNE and TCNQ to give the insertion products.

Alteration of the reaction course of organic compounds by the aid of a transition metal species is one of the most attractive subjects in organometallic chemistry.[1] We report herein that the highly reactive nature of furan toward the Diels–Alder reaction[2] is effectively reduced by the linkage to platinum complexes with σ-bond, leading to the insertion of olefins into the C–H bond of furan.

Scheme 1.



1a: $PR_3 = PMe_3$
1b: $PR_3 = PEt_3$
1c: $PR_3 = PMe_2Ph$

2a: $PR_3 = PMe_3$
2b: $PR_3 = PEt_3$
2c: $PR_3 = PMe_2Ph$

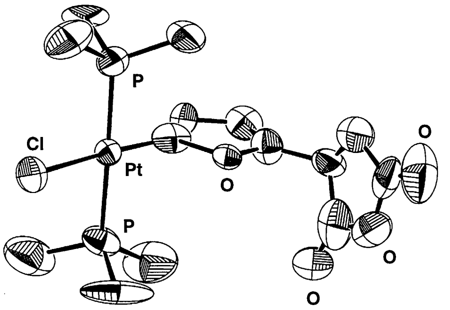


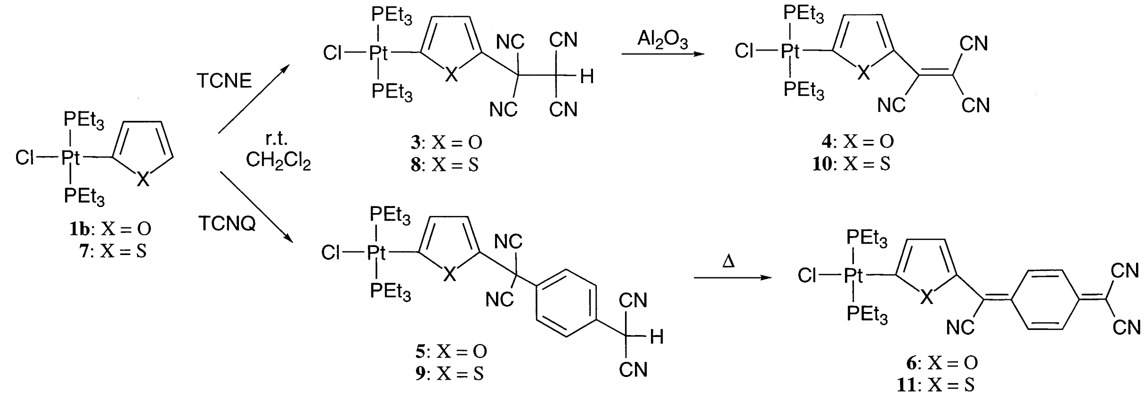
Figure 1: Molecular structure of **2a**.

Representative examples are given in Scheme 1. Reaction of 2-furanylplatinum chloride bearing two PMe_3 ligands (**1a**) with maleic anhydride (MA) (1 equiv.) under reflux in dichloromethane for 24 h formed a 1:1 adduct of the reactants (**2a**) in quantitative yield as confirmed by ^{31}P NMR analysis of the reaction solution. Complex **2a** was isolated as a yellow crystalline solid by recrystallization from a mixture of toluene and hexane (68%). The ^1H NMR spectrum exhibited three sets of doublet of doublets at δ 4.34, 3.32, and 3.14 in equal intensities, assignable to the three protons of 2-oxacyclopentane-1,3-dion-4-yl group. As to vinylic protons, only two signals were observed at δ 6.22 and 5.80, indicating the presence of di-substituted furan ring. The ^{13}C NMR data were consistent with the observations in ^1H NMR.[3]

Further identification of **2a** was carried out by X-ray crystallography.[4] As seen from the ORTEP diagram in Figure 1, complex **2a** has a 2-furanyl group substituted with 2-oxacyclopentane-1,3-dion-4-yl moiety at the 5-position. The furan ring is perpendicular to both the coordination plane around platinum and the least-square plane of the five-membered ring originated from MA.

As was found with **1a**, PEt_3- and PMe_2Ph-coordinate furanyl complexes **1b** and **1c** underwent the insertion of MA into the C–H bond at the 5-position of furanyl group to give **2b** and **2c** in 90% and 62% isolated yields, respectively (Scheme 1). Similar insertion into **1b** was also observed with tetracyanoethylene (TCNE) and 7,7,8,8-tetracyanoquinodimethane (TCNQ) under milder conditions (room temperature) (Scheme 2), while

Scheme 2.



1b: X = O
7: X = S

3: X = O
8: X = S

4: X = O
10: X = S

5: X = O
9: X = S

6: X = O
11: X = S

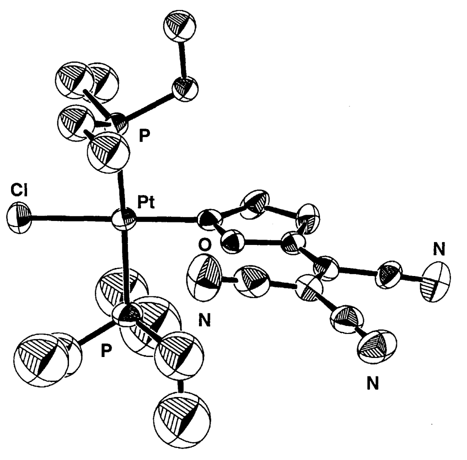


Figure 2. Molecular structure of **4**.

no reaction took place when **1b** was treated with acrolein, methyl vinyl ketone, and methyl acrylate.

In the reaction of **1b** with TCNE (Scheme 2), complex **3** was the initial product. However, this complex is unstable in a solution and gradually released HCN to provide complex **4** bearing a tricyanoethenyl side-chain. The complete elimination of HCN from **3** could be performed by the chromatographic treatment with alumina. As seen from the X-ray structure of **4** (Figure 2), the olefinic part ($C(CN)=C(CN)_2$) is nearly coplanar with the furan ring.[5]

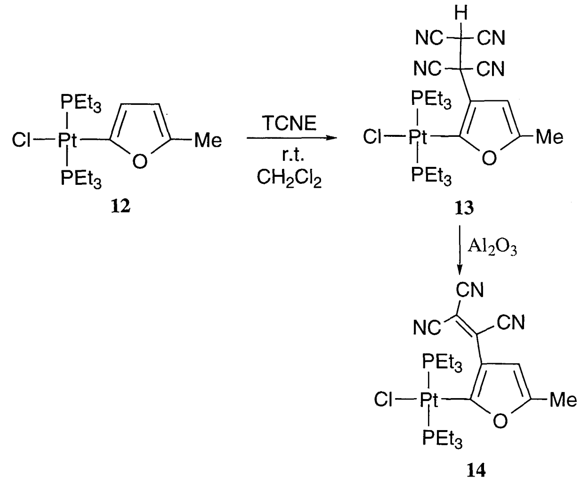
Similarly, the reaction of **1b** with TCNQ initially formed an insertion product **5** (83%), which was converted on heating into complex **6** of blue color in quantitative yield, the color being attributable to the long conjugated system including a quinodimethane structure.

2-Thienylplatinum complex (**7**) exhibited the reactivity similar to the 2-furanyl complexes, leading to the insertion products **8** and **9** and then **10** and **11** (Scheme 2).

We next examined the reaction of 2-furanyl complex substituted at the 5-position with methyl group (**12**) (Scheme 3). In this case, insertion of TCNE into a C–H bond took place at the 3-position of furanyl group and a yellow complex (**13**) was obtained in 61% yield. Treatment of **13** with alumina gave rise to the elimination of HCN to form the vinyl derivative **14** (72%).

It has been well documented that furan derivatives are good substrates toward the Diels–Alder addition to dienophiles. For example, furan readily reacts with maleic anhydride at room temperature to afford 7-oxanorbornene as the Diels–Alder product.[6] However, as we described above, such a cycloadduct was not observed in the reaction of the furan ring coordinated with platinum in a σ-bonding manner, and the selective insertion of typical dienophiles into the C–H bond takes place instead.[7] A plausible explanation of the revised reactivity is that the steric bulkiness of tertiary phosphine ligands prevents the face to face interaction between the furanyl group and dienophile required for the Diels-Alder reaction.[8] Furthermore, electron-releasing property of the platinum moiety causes increase in the electron density of furanyl group and brings about the enhanced reactivity toward the electrophilic substitution with electron-deficient olefins, leading to the formal insertion of olefins.

Scheme 3.



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References and Notes

1 J. P. Collman, L. S. Hegedus, J. R. Norton, and R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, CA (1987).

2 M. V. Sargent and F. W. Dean, *Comprehensive Heterocycle Chemistry*, ed by E. R. Katrizky and C. W. Rees, Pergamon Press, New York (1984), vol. 4.

3 Spectroscopic data for **2a**: IR (KBr) $\nu_{C=O}$ 1779 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.22 (d, J = 3.0 Hz, 1H), 5.80 (m, 1H), 4.34 (dd, J = 10.3, 6.8 Hz, 1H), 3.32 (dd, J = 18.5, 10.3 Hz) 3.14 (dd, J = 18.5, 6.8 Hz, 1H), 1.34 (vt, J = 3.9 Hz, $J_{Pt\text{-}H}$ = 29.3 Hz, 18H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 170.3 (s), 169.4 (s), 146.6 (s, $J_{Pt\text{-}C}$ = 60 Hz), 146.4 (t, $J_{P\text{-}C}$ = 13 Hz, $J_{Pt\text{-}C}$ = 1234 Hz), 112.6 (s, $J_{Pt\text{-}C}$ = 141 Hz), 110.6 (s, $J_{Pt\text{-}C}$ = 48 Hz), 41.3 (s), 34.8 (s), 13.0 (vt, J = 29.3 Hz); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ –11.7 (s, $^1J_{Pt\text{-}P}$ = 2525 Hz). Anal. Found: C, 30.44; H, 4.04; Cl, 6.20; P, 11.12%. Calcd for $C_{14}H_{23}ClO_4P_2Pt$: C, 30.70; H, 4.23; Cl, 6.47; P, 11.31%.

4 Crystal data for **2a**: $C_{14}H_{23}ClO_4P_2Pt$, FW = 547.82, orthorhombic, $P2_12_12_1$, a = 10.693(3), b = 19.043(3), c = 9.802(2) Å, V = 1996(1) Å^3, Z = 4, ρ_{calcd} = 1.823 gcm^{-3}, μ(Mo–K$_\alpha$) = 74.01 cm^{-1}, R = 0.057 and Rw = 0.052 for 199 parameters against 1427 reflections with $I > 2.0\sigma(I)$ out of 2643 unique reflections, GOF = 1.35.

5 Crystal data for **4**: $C_{21}H_{32}ClN_3OP_2Pt$, FW = 634.99, monoclinic, $P2_1/n$, a = 9.250(1), b = 35.542(6), c = 8.170(1) Å, β = 90.62(1)°, V = 2685.7(6) Å^3, Z = 4, ρ_{calcd} = 1.570 gcm^{-3}, μ(Mo–K$_\alpha$) = 54.38 cm^{-1}, R = 0.048 and Rw = 0.062 for 202 parameters against 2842 reflections with $I > 3.0\sigma(I)$ out of 4859 unique reflections, GOF = 1.60.

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7 C. H. Eugster and P. Bosshard, *Chimia*, **15**, 528 (1961); P. Bosshard, S. F. Fumagalli, R. Good, W. Treub, H. V. Philipsborn, and C. H. Eugster, *Helv. Chim. Acta*, **47**, 769 (1964).

8 An alternative reaction pathway involving Diels-Alder reaction is inconsistent with the selective formation of **13** in Scheme 3.