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Reaction of Tris(2-thienyl)phosphine with Dirhodium(II) Acetate. Orthometalation of a Heteroaromatic π-System and an Unusual Ring Rearrangement

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*Summary: The reaction of tris (2-thienyl)phosphine (**1**) with dirhodium(II) acetate in a 9:1 refluxing toluene/acetic acid mixture for 2 h leads to the formation of two metalated compounds. The structure of one of them contained two new orthometalated phosphines in a head-to-head arrangement, and, surprisingly, the metalated thiophene rings, but not the nonmetalated ones, were rearranged to a 3-thienyl structure. Both types of dirhodium compounds were assessed in a catalytic α-diazo ester transformation.*

Orthometalation of aryl phosphines is a well-known and often used reaction for the preparation of organometallic compounds.[1,2] Many catalysts of the general formula $Rh_2(O_2CR)_2(PC)_2$, PC being metalated aryl phosphines in a head to tail configuration, are accessible by direct thermal reaction of the corresponding phosphine with dirhodium tetracarboxylate.[3−7] The inherent backbone chirality of these compounds has been used for enantioselective reactions, as the racemic mixture could be separated by standard chromatographic methods.[8] Steric and electronic properties could be modified by exchanging the bridging carboxylates and/or the metalated phosphines to fine-tune catalytic activity in C−H insertion and cyclopropanation reactions resulting from diazo compound transformation.[9,10]

It was desirable to have access to a larger variety of complexes with new features. Thus, it was tempting to find out if orthometalation is limited to phenylic derivatives used so far, or it could be extended to heteroaromatic π-systems. To this end, the phosphine of choice was tris(2-thienyl)phosphine (**1**), featured by the presence of thiophene, known for its susceptibility for electrophilic reactions. On the other hand, this ligand is expected to introduce two sulfur atoms in the vicinity of the active catalytic center that could eventually increase the stability of the metal carbenoide.

The reaction of **1** and dirhodium(II) acetate, in a 1:1 molar ratio, produced exclusively the monometalated product **2**, while the same reaction in a 2:1 molar ratio led to the formation of the metalated compounds **3** and **4**, which were separated by column chromatography.[12] Multinuclear NMR investigations on the pure compounds together with crystal structure determination based on X-ray single-crystal diffraction methods revealed that one was the bis-cyclometalated product, **3**, with a head-to-tail (H−T) configuration, while the other one, **4**, was a head-to-head (H−H) product. In compounds **2** and **3** the thienyl ring was metalated at the only available carbon atom, α. We were surprised to observe that in **4** the two metalated thienyl rings had experienced rearrangement in such a way that they were linked to the phosphorus in the 3 position, while metalation took place in the α-position to sulfur in both

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[11] Single crystals of compound **4** suitable for X-ray structural determination were grown from a CH_2Cl_2/hexane/pyridine solution. Crystal data for **4**: $C_{38}H_{32}N_2O_4P_2S_6Rh_2\cdot CH_2Cl_2$: $M_r = 1125.70$, triclinic crystal system, space group $P\bar{1}$, $a = 10.3871(7)$ Å, $b = 11.2073(8)$ Å, $c = 19.7183$ Å, $\alpha = 95.5410(10)°$, $\beta = 97.4620(10)°$, $\gamma = 105.9040\ (10)°$, $V = 2167.8(3)$ Å^3, $Z = 2$, $D_{calc} = 1.725$ g/cm^3, $T = 293(2)$K, μ(Mo Kα) = 1.290 mm^{-1}, 12 457 reflections measured, 8597 independent reflections. Refinement on F^2, $R_1(F^2 > 4\sigma(F^2)) = 0.0663$, $wR_2 = 0.1482$.

[12] General procedure: $Rh_2(O_2CCH_3)_4$ (100 mg, 0.2 mmol) and **1** (120 mg, 0.43 mmol) were refluxed for 17 h in 100 mL of a 9:1 toluene/acetic acid mixture. The ^{31}P NMR of the reaction mixture indicated the presence of **2**, **3**, and **4** with spectroscopic yields of 17%, 37%, and 42%. The solvent was removed under reduced pressure, and the solid was dissolved in 5 mL of CH_2Cl_2/hexane (1:1) and transferred to a chromatography column (2.5 × 30 cm, silica gel/hexane). A first, orange band eluted with *n*-hexane/AcOEt/AcOH (10:10:0.1) was discarded. Further elution with the same mixture gave first two purple bands due to **3** and **4** and latter a gray band due to compound **2**. Compound **2**: $^{31}P\{^1H\}$ NMR ($CDCl_3$, 300 MHz): δ 0.6 (dd, $^1J_{Rh-P} = 158.0$ Hz; $^2J_{Rh-P} = 6.0$ Hz). Anal. Calc for $\mathbf{2}\cdot(CH_3COOH)_2$: C, 33.76; H, 3.20. Found: C, 33.90; H, 3.35. Compound **3**: $^{31}P\{^1H\}$ NMR ($CDCl_3$, 300 MHz): δ 4.8 (AA'XX' system, $^1J_{Rh-P} = 161.0$ Hz; $^2J_{Rh-P} = 7.7$ Hz). Anal. Calc for $\mathbf{3}\cdot(C_5H_5N)_2$: C, 43.85; H, 3.07. Found: C, 43.71; H, 3.09. Compound **4**: $^{31}P\{^1H\}$ NMR ($CDCl_3$, 300 MHz): δ 3.0 (dd, $^1J_{Rh-P} = 156.0$ Hz; $^2J_{Rh-P} = 7.5$ Hz). Anal. Calc for $\mathbf{4}\cdot(C_5H_5N)_2$: C, 43.85; H, 3.07. Found: C, 43.74; H, 3.10.

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Table 1. Catalytic Results

catalyst	solvent	T	8	9
3	CH_2Cl_2	rt	17	83
3	CH_2Cl_2	reflux	48	52
3	n-C_5H_{12}	reflux	48	52
4	CH_2Cl_2	rt	17	83
4	CH_2Cl_2	reflux	37	17
4	n-C_5H_{12}	reflux	60	40
5	CH_2Cl_2	rt	0	100
6	CH_2Cl_2	rt	0	100

phosphine ligands. The original configuration in the nonmetalated rings was maintained. No ring rearrangement was observed for the pure ligand **1**, under the same experimental conditions used in the synthesis of **4**. Thermal[13] and photochemical[14] rearrangements of substituted thiophenes have been reported.

A careful refinement of the two metalated thienyl rings allowed us to exclude any crystallographic disorder. This point was also supported by detailed 2D-NMR experiments performed on compound **4**.

The reaction of the monometalated **2** and the phosphine **1** (1:1 molar ratio) was monitored by ^{31}P NMR spectroscopy at 50 °C in a 3:1 chloroform/acetic acid mixture. Under these conditions signals of some transient species were detected, together with those assigned to the final products **3** and **4**, both formed in similar amounts. All the signals are in a very narrow range of chemical shift values, preventing any definite conclusion about the nature of the intermediate species.

Previous studies on related systems have indicated that photochemical irradiation is a suitable method to isolate reaction intermediates.[15] Longer irradiation times (1−2 h) often have also provided the bis-cyclometalated product in moderate to high yield. All these studies have confirmed that, for these reactions, the thermal and the photochemical processes follow the same reaction pathway. Following this strategy, a mixture of **2** and **1** was submitted to irradiation at room temperature. In this particular case, the conversion was complete in a very short time (<10 min) and **3** was the only reaction product. It should also be mentioned that **3** was the only detected product when dirhodium(II) acetate and **1** were irradiated, even if less than a stoichiometric amount of phosphine was used.

Dirhodium(II) complexes derived from orthometalated aryl phosphines with head-to-tail arrangement have shown active catalysts for the cyclization of α-diazo ketones, α-diazo β-keto esters, and alkyl α-diazo esters.[9,10,16]

Preliminary catalytic studies with the new catalysts **3** and **4** were carried out using methyl 2-diazoundecanoate (**7**), a substrate that exhibits competition between β-elimination and 1,5-C−H insertion reactions. Catalytic reactions were performed by addition of the dirhodium(II) catalyst to the diazo compound, both in the same solvent (diazo:catalyst =100:1; the reaction time and the temperature are indicated in Table 1). For these studies we used compound **3** as the racemic mixture. Results demonstrated that compounds **3** and **4** gave a 17% yield of the cyclization product **8** when the reaction was performed in CH_2Cl_2 at room temperature. At higher temperature the yield of cyclization increased; in refluxing CH_2Cl_2 a 48% yield was obtained using **3** and 37% for the case of **4**. Finally, a less polar solvent increased the cyclization product with isomer **4**, but no solvent effect was observed for catalyst **3**.

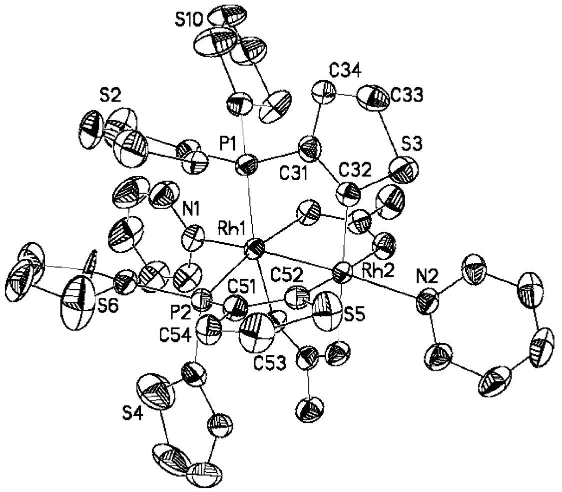
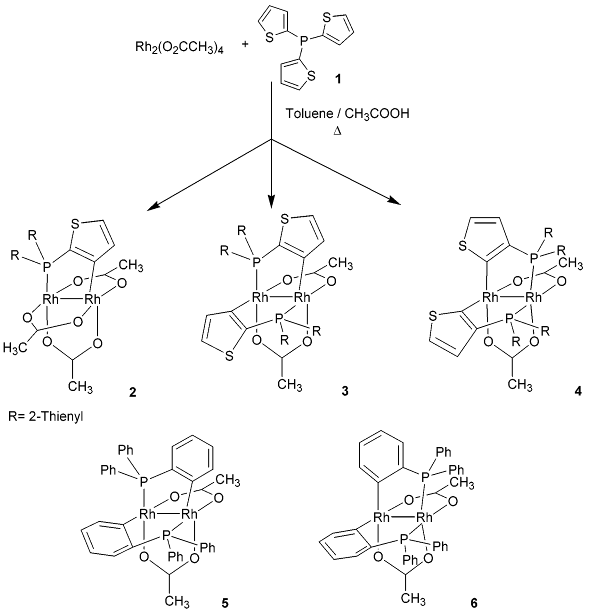
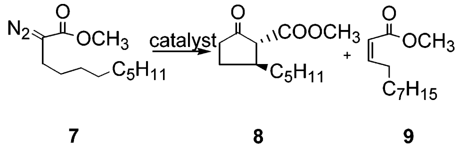


Figure 1. ORTEP drawing for **4**. Thermal ellipsoids are at the 50% probability level. Hydrogens atoms are omitted for clarity. Selected bond lengths (Å): Rh1−Rh2 = 2.5762(6), Rh1−P1 = 2.2483(16), Rh1−P2 = 2.2425(16), Rh2−C32 = 1.970(6), Rh2−C52 = 1.979(6). Selected bond angles (deg): C32−Rh2−C52 = 86.8(2), P2−Rh1−Rh2 = 87.34(4), P1−Rh1−Rh2 = 89.04(4).

Scheme 1



Scheme 2



By comparison, previous catalytic results obtained with the triphenylphosphine analogues, **5** (H−T)[3] and **6** (H−H),[17] have been included in Table 1. No C−H

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insertion product, but the elimination product **9**, is obtained in the transformation of diazo **7** promoted by these two rhodium(II) complexes. We have reported that **6** is not active in the transformation of other types of diazo compounds.[10]

Further investigations on the mechanism of the orthometalation reaction and the catalytic properties of the metalated products are ongoing.

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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