

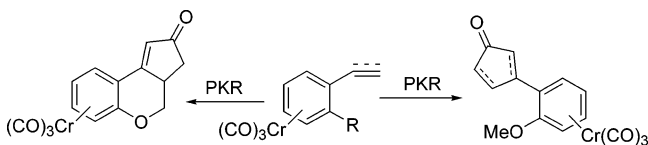
Arene–Chromium Tricarbonyl Complexes in the Pauson–Khand Reaction

Marta Rosillo, Gema Domínguez, Luis Casarrubios,[†] and Javier Pérez-Castells*

Universidad San Pablo-CEU, Departamento de Química, Facultad de Farmacia, Urb. Montepríncipe, 28668 Boadilla del Monte, Madrid, Spain

jpercass@ceu.es

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We show the use of arene–chromium tricarbonyl complexes in intra- and intermolecular Pauson–Khand reactions. Both styrene and ethynylbenzene complexes react with alkynes and olefins. The synthesis of enynes connected through chromium-complexed aromatic rings is developed. The intramolecular Pauson–Khand reaction occurs in a totally diastereoselective manner.

1. Introduction

The chemistry of arene–chromium tricarbonyl complexes¹ has received much attention as they can suffer efficient nucleophilic additions and ring lithiations and act as catalysts in hydrogenations and double-bond shift reactions. In addition, the (CO)₃ substitution allows an efficient stabilization of both positive and negative benzylic charges.² This fact has been the basis for some syntheses of complex molecules.³ One interesting aspect of these compounds is they are planar chiral when they are ortho or meta unsymmetrically disubstituted. This has led to the development of different enantioselective syntheses of these compounds.⁴ Optically active planar complexes can also be obtained by resolution of the corresponding diastereomers.⁵ The presence of the Cr(CO)₃ substituent generates a great facial selectivity in the aromatic ring. This can be used for chiral catalysis

[†] Present address: Centro de investigación Lilly S. A. Avda. de la industria 30. 28108 Alcobendas, Madrid, Spain.

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and in the synthesis of natural products where chromium complexes act as chiral building blocks.⁶

Arene–chromium tricarbonyl complexes have hardly been used in Pauson–Khand reactions.⁷ With the exception of an early example by Pauson in the 1970s,⁸ the only related precedent is by Kündig, who used these complexes as starting materials for the stereoselective synthesis of an enyne, by means of a nucleophilic addition to the aromatic complex and reaction with an appropriate electrophile.⁹ This enyne was used in a PKR. We have shown the utility of aromatic enynes in the PKR both based on phenyl or on indole rings.¹⁰ This chemistry allows the synthesis of polycyclic compounds related with natural products. Herein, we report the novel use of arene–chromium carbonyl complexes in inter- and intramolecular Pauson–Khand reactions.

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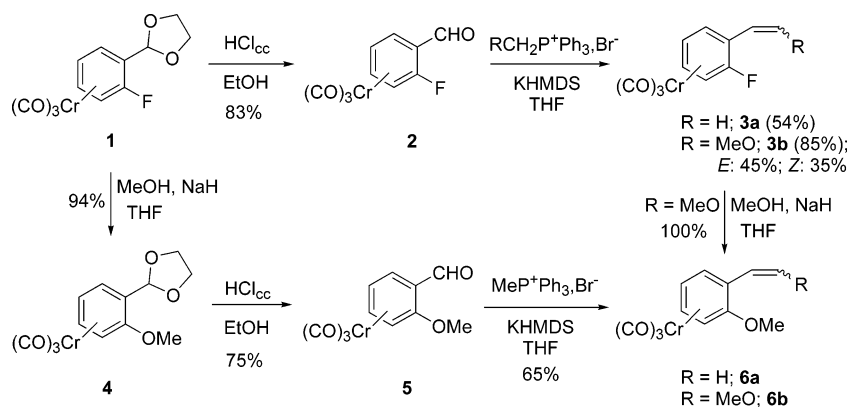
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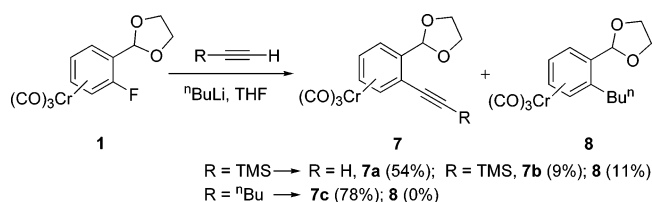
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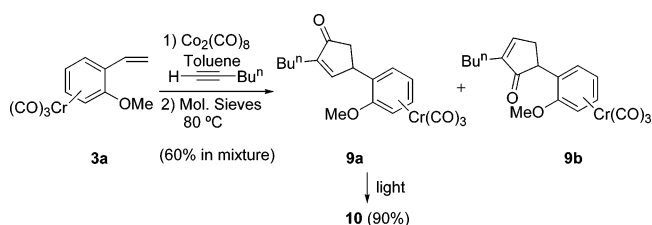
SCHEME 1



SCHEME 2



SCHEME 3



2. Results and Discussion

The synthesis of substrates for the intermolecular PKR containing a chromium-complexed aromatic ring started from complex **1** which was prepared according to literature procedures from 2-fluorobenzaldehyde.¹¹ Styrene derivatives were obtained from **1** as summarized in Scheme 1 by means of deprotection of the acetal and Wittig reaction. KHMDS was used as the base, giving **3a** and **3b** with good yields, the latter as a mixture of *E/Z* isomers which could be separated by chromatography. In addition, the fluoride in **1** was substituted by methoxide in high yield giving **4**, which was transformed into **6a** using the same methodology. A 3:2 mixture of *E/Z* isomers of compound **6b** was obtained from a mixture of **3b** isomers by replacement of the fluoride. This synthesis gave better yields than the alternative transformation of **5** into **6b** via a Wittig reaction.

The synthesis of the complementary substrates bearing a triple bond was effected by nucleophilic attack of different acetylides on compound **1**. Thus, the reaction of **1** with trimethylsilylacetylide afforded the desilylated compound **7a** (54%) as the major product, along with small amounts of **7b** and **8**. We have tried to avoid the formation of **8** using other bases such as *t*-BuLi, NaH, or KHMDS, but the yields of the reaction were lower (35%, 42%, and 47%, respectively, in compound **7a**), so we adjusted the ratio of *n*-BuLi to 1.1 equiv in order to minimize the formation of **8** (11%). On the other hand, the lithium salt of 1-hexyne reacted cleanly giving **7c** in 78% yield (Scheme 2).

Compounds **3** and **6** were reacted with 1-hexyne. The reactions were carried out in degassed toluene using three different promoters: heat (conditions A), NMO (conditions B), and molecular sieves (conditions C). Only the latter conditions allowed the conversion of **3a** into a

mixture of Pauson–Khand products **9a,b**. The first two promoters led to extensive decomposition of the starting materials. Compounds **9a** and **9b** are the two regioisomers coming from the reaction of the alkene with both possible orientations. Compound **9a** could be isolated and completely characterized. This compound was decomposed by exposure to light, giving **10** (Scheme 3). Compound **3a** did not react with 3-hexyne or with 1-phenylacetylene in any of the above reaction conditions. Noncomplexed styrenes usually give poor conversions in the PKR.¹²

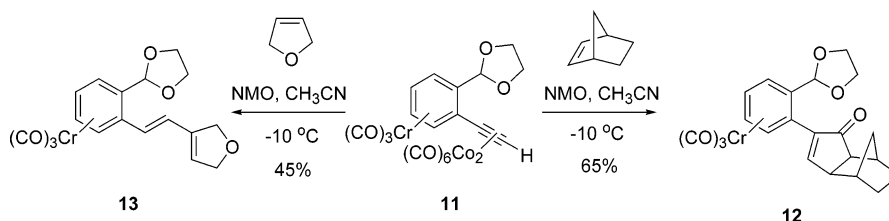
Alkynes **7** gave poor results under typical PKR conditions. Thus, compound **7a** under conditions B described above gave 25% of the PK adduct. To improve this result, we prepared and isolated heterobimetallic complex **11**. The proximity of the metals prompted us to make a DRX study of this complex to see possible interactions between both metals. The ORTEP structure shows a typical structure for both the chromium and the cobalt bonding. The Co–Co distance is 2.47 Å, in the normal range for these kind of complexes.¹³ The reaction of **11** with norbornene gave **12** as the only reaction product. In this case TMANO promotion at -10 °C was used reaching 65% yield. Other reaction conditions at elevated temperatures led to decomposition of the initial complex. The assignment of the structure of **12** was done by NOE experiments, and we concluded it was the *exo* adduct. On the other hand, the reaction of **7a** with 2,5-dihydrofuran under the same conditions gave **13** as the only reaction product. Compound **13** is the result of a well-known side reaction that implies the insertion of the alkyne into a

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SCHEME 4



SCHEME 5

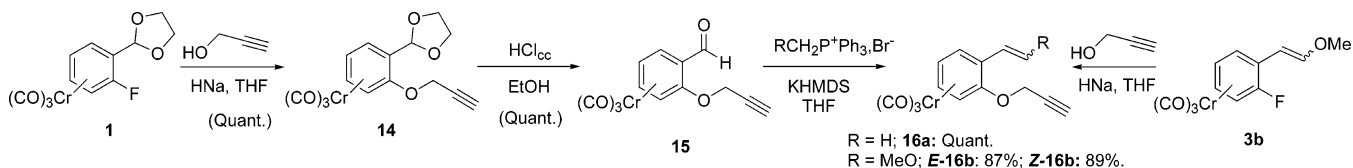


TABLE 1. Intramolecular PKR in Chromium Tricarbonyl Complexes

substrate	conditions	promoter	T (°C)	yield (%)	
				17a,b	18
16a	A		110	<10	
16a	B	NMO	-10	56 (30) ^a	
16a	C	4 Å mol. sieves	80	60 (50) ^a	
16a	D	NMO/4 Å mol. sieves	rt	85 (60) ^a	
E-16b	D	NMO/4 Å mol. sieves	rt	45 (25) ^{a,b}	12
Z-16b	D	NMO/4 Å mol. sieves	rt	52 (25) ^{a,b}	18
E-16b	C	4 Å mol. sieves	80	44 (35) ^{a,b}	28
Z-16b	C	4 Å mol. sieves	80	39 (35) ^{a,b}	32

^a Yields in parentheses correspond to the reaction of the parent uncomplexed enynes for each reaction conditions, taken from ref 10a. ^b These yields correspond to reactions of the parent uncomplexed mixtures of *E/Z* isomers.

C–H bond of the olefin.¹⁴ The stereochemistry of **13** was assigned by the value of the coupling constant, which was in the typical range for *trans* isomers ($J = 18.1$ Hz) (Scheme 4). Reactions with 1-heptene or with dihydropyrene were unsuccessful under all the conditions tested. These olefins are much less reactive in intermolecular PKR as shown by numerous experimental studies supported by theoretical calculations.¹⁵

Next, we addressed the synthesis of enynes complexed to chromium. Compound **1** was reacted with propargylic alcohol to give quantitatively compound **14**. Hydrolysis of the dioxolane and Wittig reaction gave the desired enynes **16**. In the case of compounds **16b**, the 2:1 *E/Z* mixture could be separated by chromatography. Alternatively complexes *E*- and *Z*-**3b** could be reacted separately with propargyl alcohol to give *E*- and *Z*-**16b** with good yields (Scheme 5).

Compound **16a** was reacted in the three reaction conditions mentioned above (Table 1). We reached an only reaction product in the three cases corresponding to structure **17a**. This implies the isomerization of the emerging double bond as we had observed with similar but not complexed to chromium substrates.¹⁰ The

obtention of an only compound implies the total diastereoselection of the reaction. Although conditions B and C gave compound **17a** in good yields the best results were obtained by a combination of both promoters (molecular sieves and NMO, conditions D) reaching 85% yield. These latter conditions were used with both *E*-**16b** and *Z*-**16b**. In these cases, however, we obtained mixtures of the expected adduct **17b** with the diene **18**. Due to the double bond shift, both isomers of the starting product gave the same cyclopentenone **17b**, as an only diastereoisomer. The formation of a byproduct like **18** implies the insertion of the triple bond into a C–H bond of the olefin. This is a common reaction in certain PK processes but with enynes, the formation of six membered rings is usually observed. However in our case oxepine **18** was obtained. When using conditions C with both isomers of **16b** the amount of **18** increased. The stereochemistry (*E*) of the exocyclic double bond in **18** was established by NOE experiments.

In a previous work from our group,^{10a} we had reacted the related noncomplexed to chromium substrates. It is interesting to note that these chromium-complexed enynes react with higher yields. The oxepine we have isolated in the reaction of **16b** was not detected in the reaction of the uncomplexed enyne.

In conclusion, the reactivity of chromium complexed arenes in the PKR has been explored. The complexes exhibit high diastereoselectivity degrees although in general, they have low reactivity. The best results were achieved with intramolecular reactions.

Experimental Section

Preparation of 7a and 7b. To a stirred solution of ethynyltrimethylsilane (2.42 g, 24.7 mmol) in THF (30 mL) was added *n*-BuLi (12.3 mL, 1.6 M in hexane, 19.7 mmol) at -78 °C. After the mixture was stirred for 30 min, complex **1** (3.00 g, 9.9 mmol) in THF (40 mL) was added dropwise. The reaction mixture was allowed to warm to room-temperature overnight and was quenched at 0 °C with aqueous NH₄Cl followed by extraction (Et₂O/H₂O). The aqueous phase was washed with ether, and the combined organic layers were dried with Na₂SO₄ and filtered. Concentration, followed by column chromatography (hexane/AcOEt 6:1), afforded 1.65 g (54%) of complex **7a** as a yellow solid (mp 113–114 °C (hexane)), 322 mg (9%) of **7b** as a yellow oil, and 340 mg (11%) of subproduct **8** unpurified with **7b**, which was not characterized. See the Supporting Information for spectroscopic data of **7a,b**.

2-Butyl-4-(2-methoxyphenyl)cyclopent-2-enone–Chromium Tricarbonyl, 9a. Hex-1-yne (0.085 mL, 0.74 mmol) and complex **3a** (100 mg, 0.37 mmol) were solved in degassed toluene (10 mL) at room temperature under argon. To this solution was added $\text{Co}_2(\text{CO})_8$ (253 mg, 0.74 mmol), and the resulting mixture was stirred for 1 h until total complexation of the alkyne (TLC). Then, powdered 4 Å molecular sieves (8 times the mass of the complex) were added to the reaction mixture. The reaction was then heated at 80 °C and stirred overnight. The crude was filtered through diatomaceous earth and the solvent evaporated under vacuum. The residue was purified by column chromatography (hexane/AcOEt 20:1 to 4:1) giving 74 mg (60%) of a pure mixture of compounds **9a** and **9b**. A small amount of **9a** could be obtained separately from the chromatography and was characterized. Data for **9a**: $^1\text{H NMR}$ δ 0.92 (t, 3H, $J = 6.6$ Hz), 1.34–1.36 (m, 2H), 1.47–1.49 (m, 2H), 2.17–2.22 (m, 2H), 2.58–2.66 (m, 1H), 3.16–3.26 (m, 1H), 3.78 (s, 3H), 3.95–3.98 (m, 1H), 4.90 (t, 1H, $J = 6.3$ Hz), 5.09 (d, 1H, $J = 6.6$ Hz), 5.29 (d, 1H, $J = 6.1$ Hz), 5.54 (t, 1H, $J = 6.3$ Hz), 7.41 (bs, 1H); $^{13}\text{C NMR}$ δ 232.3, 207.5, 156.7, 94.0, 93.9, 85.4, 73.7, 56.1, 43.1, 37.1, 29.7, 24.7, 22.4, 13.8. (Some of quaternary carbon signals were too weak to be observed); IR (KBr) ν 1970, 1890, 1700 cm^{-1} . Data for **9b**, from a spectrum of the mixture: $^1\text{H NMR}$ δ 0.92 (t, 3H, $J = 6.6$ Hz), 1.29–1.39 (m, 2H), 1.43–1.51 (m, 2H), 2.19–2.26 (m, 2H), 2.83–2.90 (m, 1H), 3.07–3.19 (m, 2H), 3.66 (s, 3H), 4.87 (t, 1H, $J = 6.3$ Hz), 5.07 (d, 1H, $J = 6.6$ Hz), 5.57 (t, 1H, $J = 6.1$ Hz), 5.63 (d, 1H, $J = 6.1$ Hz), 6.84–6.93 (m, 1H).

(3aS*,4S*,7R*,7aS*)-2-(2-[1,3]Dioxolan-2-ylphenyl)-3a,4,5,6,7,7a-hexahydro-4,7-methanoinden-1-one–Chromium Tricarbonyl, 12. A 0.7 mmol (400 mg) sample of the complex **11** was dissolved in dry acetonitrile (10 mL) at room temperature under argon. This solution was cooled to –10 °C with an ice/salt bath, and 470 mg (4.0 mmol) of NMO and a solution of 950 mg (1.0 mmol) of norbornene in 5 mL of acetonitrile were added. After 3 h of stirring, the mixture was filtered through diatomaceous earth, the solvent was evaporated under vacuum, and the crude product was purified by chromatography (hexane/AcOEt 4:1). A total of 190 mg (65%) of **12** was obtained as a yellow solid, mp 142–143 °C (hexane). No NOE increments were observed when irradiating the 4 and 5 protons of the cyclopentenone ring on the methylene protons of the bridge: $^1\text{H NMR}$ δ 1.03–1.15 (m, 2H), 1.27–1.42 (m, 2H), 1.57–1.79 (m, 2H), 2.32–2.38 (m, 2H), 2.50 (d, 1H, $J = 3.3$ Hz), 2.77–2.80 (m, 1H), 3.92–4.17 (m, 4H), 5.31–5.41 (m, 3H), 5.59 (s, 1H), 5.71 (dd, 1H, $J = 5.5$ Hz, $J = 1.6$ Hz), 7.77 (d, 1H, $J = 3.3$ Hz); $^{13}\text{C NMR}$ δ 232.3, 207.3, 166.1, 143.0, 106.6, 100.9, 99.9, 93.9, 91.7, 91.0, 89.8, 65.9, 65.6, 54.2, 48.4, 39.5, 38.2, 31.3, 29.2, 28.2; IR (KBr) ν 3010, 1970, 1890, 1700 cm^{-1} ; Anal. Calcd for $\text{C}_{22}\text{H}_{20}\text{CrO}_6$: C, 61.11; H, 4.66. Found: C, 61.29; H, 4.75.

3a,4-Dihydro-3H-cyclopenta[c]chromen-2-one–Chromium Tricarbonyl, 17a. To a solution of 250 mg (0.8 mmol) of

enone **16a** in 25 mL of toluene under argon was added 350 mg (1.0 mmol) of $\text{Co}_2(\text{CO})_8$. The resulting mixture was stirred until total complexation of the alkyne (TLC). The reaction was then cooled to –10 °C with an ice/salt bath, and 8 times the mass of the enyne of powdered 4 Å molecular sieves and a suspension of 250 mg (3.4 mmol) of Me_3NO in 5 mL of toluene were added. After 12 h of stirring, the mixture was filtered through diatomaceous earth and the solvent evaporated under vacuum. The residue was purified by column chromatography (hexane/AcOEt 2:1). The product **17a** was recovered in 85% (240 mg) as a red solid: mp 160–162 °C (hexane); $^1\text{H NMR}$ δ 2.15 (dd, 1H, $J_1 = 17.8$ Hz, $J_2 = 4.7$ Hz), 2.68 (dd, 1H, $J_1 = 17.8$ Hz, $J_2 = 7.3$ Hz), 3.16–3.27 (m, 1H), 3.93 (dd, 1H, $J_1 = 12.9$ Hz, $J_2 = 10.7$ Hz), 4.51 (dd, 1H, $J_1 = 10.7$ Hz, $J_2 = 5.8$ Hz), 5.11 (t, 1H, $J = 6.3$ Hz), 5.36 (d, 1H, $J = 6.6$ Hz), 5.65 (t, 1H, $J = 6.3$ Hz), 5.84 (d, 1H, $J = 7.1$ Hz), 6.30 (d, 1H, $J = 2.2$ Hz); $^{13}\text{C NMR}$ δ 231.2, 204.5, 166.3, 137.3, 123.4, 94.4, 91.8, 85.3, 81.6, 80.5, 69.8, 37.4, 36.6; IR (KBr) ν 1980, 1950, 1910, 1880 cm^{-1} . Anal. Calcd for $\text{C}_{15}\text{H}_{10}\text{CrO}_5$: C, 55.91; H, 3.13. Found: C, 56.05; H, 3.46.

Preparation of 17b and 18. The same procedure reported for the preparation of complex **17a** was used, from 290 mg (0.89 mmol) of complex **E-16a**, giving 145 mg (45%) of complex **17b** as a red oil and 35 mg (12%) of **18** as a yellow oil.

1-Methoxy-3a,4-dihydro-3H-cyclopenta[c]chromen-2-one–Chromium Tricarbonyl, 17b: $^1\text{H NMR}$ δ 2.07 (dd, 1H, $J_1 = 17.9$ Hz, $J_2 = 4.1$ Hz), 2.60 (dd, 1H, $J_1 = 18.1$ Hz, $J_2 = 6.6$ Hz), 2.94–3.03 (m, 1H), 3.86 (dd, 1H, $J_1 = 12.4$ Hz, $J_2 = 10.7$ Hz), 4.15 (s, 3H), 4.48 (dd, 1H, $J_1 = 10.4$ Hz, $J_2 = 5.5$ Hz), 5.03 (t, 1H, $J = 6.3$ Hz), 5.34 (d, 1H, $J = 6.6$ Hz), 5.58 (td, 1H, $J_1 = 6.6$ Hz, $J_2 = 1.4$ Hz), 6.49 (dd, 1H, $J_1 = 6.6$ Hz, $J_2 = 1.1$ Hz); $^{13}\text{C NMR}$ δ 232.2, 198.9, 150.1, 139.0, 137.0, 94.4, 93.2, 85.1, 83.2, 81.8, 70.2, 58.6, 35.6, 30.4; IR (neat) ν 3020, 1970, 1890, 1700 cm^{-1} . Anal. Calcd for $\text{C}_{16}\text{H}_{12}\text{CrO}_6$: C, 54.55; H, 3.43. Found: C, 54.45; H, 3.30.

(E)-5-Methoxymethylene-2,5-dihydrobenzo[b]oxepine–chromium tricarbonyl, 18: $^1\text{H NMR}$ δ 3.73 (s, 3H), 4.78 (d, 1H, $J = 6.6$ Hz), 4.92–5.08 (m, 3H), 5.20 (d, 1H, $J = 6.6$ Hz), 5.36–5.40 (m, 2H), 6.04 (d, 1H, $J = 7.1$ Hz), 6.06 (bs, 1H); $^{13}\text{C NMR}$ δ 234.0, 150.2, 136.6, 134.3, 115.4, 114.0, 102.3, 92.9, 92.3, 85.8, 81.5, 68.0, 61.0; IR (neat) ν 3010, 1960, 1880, 1640 cm^{-1} . Anal. Calcd for $\text{C}_{15}\text{H}_{12}\text{CrO}_5$: C, 55.56; H, 3.73. Found: C, 55.80; H, 3.93. NOE: $\text{CH}_3\text{O} \rightarrow \text{H}_4$, 2.5%; $\text{H-C(OMe)=C} \rightarrow \text{H}_6$, 7%.

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Supporting Information Available: Spectral data for all new compounds and ORTEP drawing and X-ray crystallographic data for **11** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(14) For reactivity of phenylacetylene in intermolecular PKRs, see ref 12c.

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