Reactions of Complex Ligands, LXXII[◇]

Intermolecular Pauson-Khand Reactions of Ethyl 2-Phenylethynylcyclopropanecarboxylates and [Amino(*trans*-2-phenylethynylcyclopropyl)methylidene]pentacarbonylchromium(0)☆

Oliver Kretschik[a,b], Martin Nieger[c], and Karl Heinz Dötz*[a]

Institut für Organische Chemie und Biochemie der Universität Bonn[a],
Gerhard-Domagk-Straße 1, D-53121 Bonn, Germany

Department of Chemistry, University of California[b],
Los Angeles, CA 90095-1569, U.S.A.
E-mail: Kretsch@chem.ucla.edu

Institut für Anorganische Chemie der Universität Bonn[c],
Gerhard-Domagk-Straße 1, D-53121 Bonn, Germany

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The intermolecular Pauson-Khand reactions of ethyl *trans*-2-phenylethynylcyclopropanecarboxylate (**1t**) and [amino(*trans*-2-phenylethynylcyclopropyl)methylidene]pentacarbonylchromium (**9**) with norbornene lead to ester and metal carbene functionalized *exo*-tricyclodecenones **3**–**6** and **13**–**16**, respectively, in moderate to high yields. The incorporation of the alkyne is moderately regioselective but less diastereoselective. Pairs of diastereomers are isolated after column chromatography, which can subsequently be separated by recrystallization. The minor diastereomer **3** and the major diastereomer **15** are characterized by X-ray structure analysis.

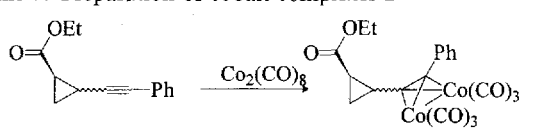
As Fischer-type carbene complexes have become valuable reagents for stereoselective carbon-carbon bond formation[2], we were interested in the modification of carbene ligands and aimed at the incorporation of more complex functionalities into the carbene ligand. Recently, we reported the synthesis of diastereomerically pure (2-ethynylcyclopropyl)methoxycarbene complexes of chromium and tungsten[3] and on the modification of the carbon-carbon triple bonds in such complexes via chromium-mediated benzannulation reactions[1]. The strong donor properties of the cyclopropyl group[4] render cyclopropyl carbene complexes more thermostable; thus, we extended our studies to reactions that require more drastic conditions such as the cobalt-mediated Pauson-Khand reaction[5]. This type of formal [2 + 2 + 1] cycloaddition allows a one-pot synthesis of cyclopentenones, which are of considerable biological interest[6]. Aminocarbene complexes have been found to undergo *intra*molecular Pauson-Khand reactions under surprisingly mild conditions[7]. We now report on *inter*molecular Pauson-Khand reactions using ester and metal carbene functionalized alkynes which exhibit similar electronic characteristics.

[◇] Part LXXI: Ref.[1].

[2 + 2 + 1] Cycloaddition with Ethyl Cyclopropanecarboxylate 1 and Norbornene

In order to explore the regio- and diastereoselectivity of the Pauson-Khand reaction using cyclopropyl-substituted alkynes, ethyl cyclopropanecarboxylates **1c**, **t** were reacted with a slight excess of dicobaltoctacarbonyl at room temperature. Chromatography on silica gel afforded the diastereomerically pure cobalt complexes **2c**/**2t** as dark-red oils (Scheme 1) in high yields.

Scheme 1. Preparation of cobalt complexes **2**



1c,t → **2c** (95 %), **2t** (91 %)

Due to the lability of pentacarbonyl carbene complexes towards oxidants[8] the following [2 + 2 + 1] cycloadditions were performed under nonoxidative conditions (without promoting reagents such as trimethylamine *N*-oxide etc.). Warming of the cobalt complex **2t** with five equivalents of norbornene in toluene at 90 °C for 66 h afforded a mixture of four cycloaddition products with identical molecular

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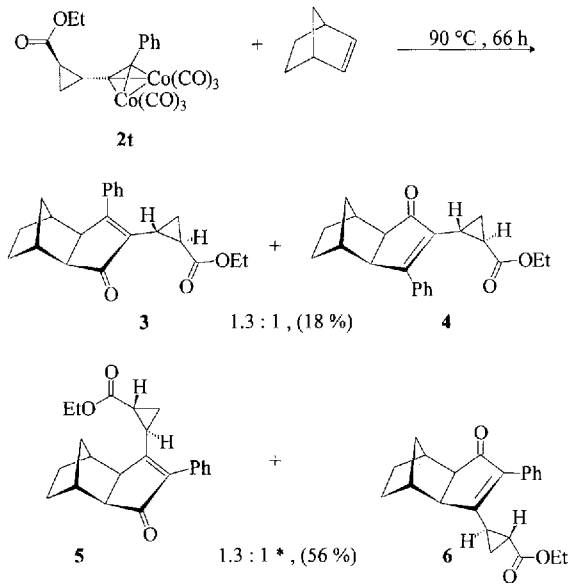
masses. Chromatographic workup on silica gel furnished a 74% overall yield of two pairs of tricyclodecenones **3/4** and **5/6** in a ratio of **3/4**:**5/6** = 1:3.1 (Scheme 2). The diastereomers **3** and **4** could be separated by fractional crystallization from hexane.

Scheme 2. [2 + 2 + 1] Cycloaddition of complex **2t** with norbornene

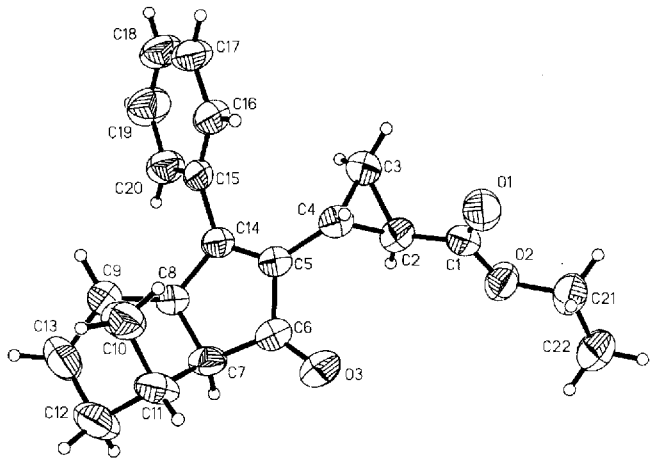


Norbornene undergoes Pauson-Khand reactions exclusively under formation of *exo*-fused tricyclodecenones[9]; thus, the formation of four isomers indicates the incorporation of the carbon-carbon triple bond to form both possible regioisomers as expected for unsymmetrical alkynes. Generally the larger alkyne substituent is incorporated predominantly adjacent to the cyclopentenone carbonyl group[10]. In our case, the compounds with identical R_f values [R_f (**3/4**) = 0.30; R_f (**5/6**) = 0.25] show very similar NMR spectra but by means of ^{13}C-NMR spectroscopy two pairs of diastereomers can be clearly distinguished due to their different substitution pattern at the new carbon-carbon double bond within the cyclopentenone ring. Thus, the products with identical R_f values can be regarded as regioisomers with respect to the incorporation of the alkyne. Since spectroscopic means did not allow an unambiguous assignment of the relative configurations in the cycloaddition products **3**–**6**, the structure of one of the minor diastereomers (**3**) was established by X-ray structure analysis (Figure 1).

The molecular structure of **3** confirms the formation of an *exo*-fused tricyclodecenone and the incorporation of alkyne **2t** with its cyclopropyl group, as the smaller substituent (R_S), being placed adjacent to the carbonyl group of the cyclopentenone ring and the phenyl substituent being incorporated next to the ring junction, as expected for the larger substituent (R_L) in the minor regioisomer.

As a consequence of the *trans* configuration in the three-membered ring, the ester group does not affect the steric demand of the cyclopropyl system during the cyclization. Following the experimental protocol for the preparation of

Figure 1. Molecular structure of **3**; selected bond lengths [pm] and angles [°]: C(1)–O(1) 120.0(3), C(1)–O(2) 132.5(3), C(2)–C(3) 149.6(4), C(2)–C(4) 150.7(4), C(3)–C(4) 148.9(4), C(5)–C(14) 134.6(4), C(6)–O(3) 122.3(3), C(7)–C(8) 154.7(4); C(6)–C(7)–C(11) 113.9(3), C(14)–C(8)–C(9) 113.5(2), C(14)–C(5)–C(6) 109.4(2)



tricyclodecenones **3**–**6**, the *cis* diastereomer **2c** gave only a 13% overall yield of the corresponding Pauson-Khand products after 144 h. The cycloaddition products were identified by means of GC-MS analysis, but – due to the unsatisfactory yields – were not fully characterized. Obviously, the *cis* configuration in the three-membered ring enhances the steric demand of the cyclopropyl system and thus hampers the coordination of norbornene to the cobalt template.

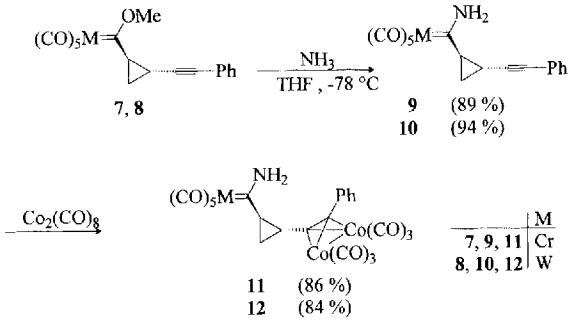
[2 + 2 + 1] Cycloaddition with Hexacarbonyl-μ-η-{[amino(*trans*-2-phenylethynylcyclopropyl)methylidene] pentacarbonylchromium(0)}dicobalt(Co–Co) (11) and Norbornene

We were interested in the modification of carbene ligands and extended our studies to the chromium carbene complex **11** as an alkyne component for the Pauson-Khand reaction with norbornene. In view of the conditions required for the synthesis of compounds **3**–**6** (90 °C), the more thermostable amino carbene complexes were used instead of methoxy carbene complexes as the "isolobal analogues" of ester **2t**. Considering the low yield in the reaction of **2c** with norbornene, we focussed on the *trans*-cyclopropyl complexes.

Upon addition of liquid ammonia to methoxy carbene complexes of chromium and tungsten **7** and **8** at –78 °C in THF, yellow amino carbene complexes **9** and **10** were formed, which underwent complexation with dicobaltoctacarbonyl at room temperature to give complexes **11** and **12** in high yields as black solids after chromatographic workup (Scheme 3).

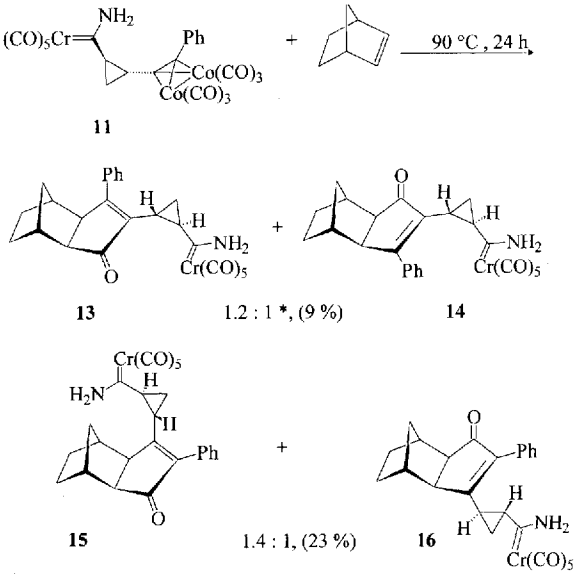
Following the experimental protocol for the preparation of tricyclodecenones **3**–**6**, complex **11** was treated with norbornene for 24 h to give compounds **13**–**16** (Scheme 4). Chromatographic workup on silica gel afforded a 32% overall yield of two pairs of cyclopentenone derived amino carbene complexes **13/14** and **15/16** in a ratio of **13/14**:**15/16** = 1:2.6, which is similar to that observed for the [2 + 2 + 1]

Scheme 3. Preparation of amino carbene complexes of chromium and tungsten **9**–**12**



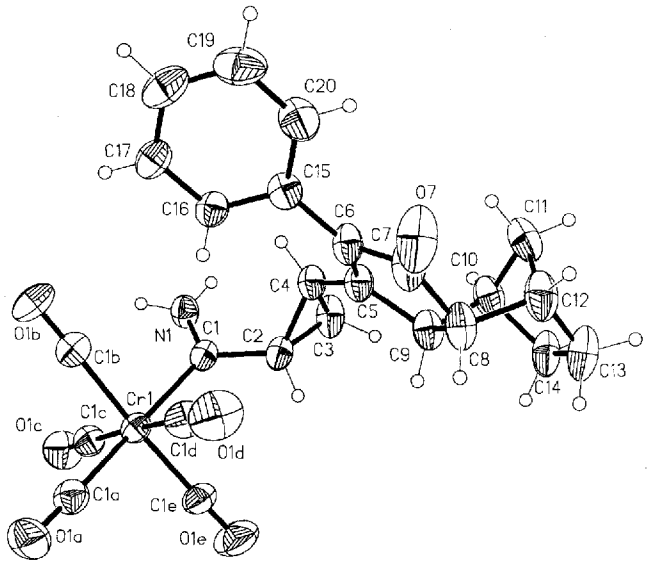
cycloaddition of norbornene with cyclopropylcarboxylate **2t**. In addition, 15% of unreacted starting material **11** was recovered.

Scheme 4. [2 + 2 + 1] Cycloaddition of amino carbene complex **11** with norbornene



The complexes within a pair of diastereomers exhibit the same regiochemistry with respect to the incorporation of the alkyne into the cyclopentenone skeleton. The diastereomers **15** and **16** could be separated by fractional crystallization from hexane/dichloromethane at room temperature. To ascertain whether the formation of diastereomers **13**–**16** was comparable with our results obtained from the reaction of norbornene with cyclopropylcarboxylate **2t**, the structure of the main product of the major pair of diastereomers (**15**) was established by X-ray crystal structure analysis (Figure 2). In comparison with the minor carboxylate diastereomer **3**, the molecular structure of the major metal carbene diastereomer **15** shows the opposite regiochemistry. Thus, the *trans*-disubstituted cyclopropane skeleton which bridges the carbene acceptor moiety and the *exo*-fused tricyclodecenone system, again behaves as the small substituent compared with the phenyl group. These examples demonstrate that the intermolecular Pauson-Khand reaction generally tolerates multiple-functionalized alkynes bearing bulky organometallic substituents.

Figure 2. Molecular structure of **15**; selected bond lengths [pm] and angles [°]: Cr(1)–C(1) 207.4(5), C(1)–N(1) 130.4(6), C(2)–C(3) 148.8(7), C(2)–C(4) 153.7(6), C(3)–C(4) 150.5(6), C(5)–C(6) 135.4(6), C(7)–O(7) 120.8(6); Cr(1)–C(1)–C(2) 121.2(3), Cr(1)–C(1)–N(1) 124.8(3), C(5)–C(9)–C(10) 113.5(4), C(7)–C(8)–C(12) 112.0(5)



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Experimental Section

All operations, except for the isolation of compounds **3**–**6**, were performed under argon. Solvents were dried by distillation from sodium-potassium alloy and sodium hydride; petroleum ether (PE) 40–60 °C. Silica gel (Merck; 0.063–0.200 mm) was degassed at high vacuum and stored under argon. – ^{1}H and ^{13}C NMR: Bruker AMX-500, AM-400, AM-250. Chemical shifts refer to those of residual solvent signal based on $\delta_{TMS} = 0.00$. – FT-IR: Nicolet Magna 550. – MS: Kratos MS 50 and Hewlett Packard 5972. – Melting points: Büchi SMP 20, uncorrected. – Elemental analysis: Heraeus CHN-O-Rapid. Compounds **1c**, **1t**, **7**, and **8** were prepared as previously described[3].

General Procedure for the Preparation of [Amino(trans-2-phenylethynylcyclopropyl)methylidene]pentacarbonyl Complexes **9**, **10**: To a solution of 5 mmol of pentacarbonylmethoxymethylidene complex (**7** or **8**) in 50 ml THF, a solution of 10 ml of liquid ammonia in 10 ml THF was added at −78 °C. After stirring at this temperature for 10 min, the mixture was allowed to warm to room temp. and the solvent was removed. Chromatography (−5 °C, silica gel, petroleum ether/dichloromethane, 1:1) of the yellow residue gave yellow solids.

[Amino(trans-2-phenylethynylcyclopropyl)methylidene]pentacarbonylchromium(0) (**9**): Yield 1.61 g (89%), $R_f = 0.33$ (PE/CH_2Cl_2, 1:1). – IR (hexane): $\tilde{\nu}$ [ν(C=O)] = 2059 cm^{-1} (m, A_1), 1976 (w, B_1), 1946 (vs, E), 1925 (s, A_1). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.56 (ddd, $^3J_{cis} = 9.00$ Hz, $^3J_{trans} = 6.45$ Hz, $^2J = 5.28$ Hz, 1H, 3-H), 1.62 (ddd, $^3J_{cis} = 8.41$ Hz, $^3J_{trans} = 6.26$ Hz, $^2J = 5.28$ Hz, 1H, 3-H), 2.02 (ddd, $^3J_{cis} = 9.00$ Hz, $^3J_{trans} = 6.26$ Hz, $^3J_{trans} = 4.69$ Hz, 1H, 2-H), 3.01 (ddd, $^3J_{cis} = 8.41$ Hz, $^3J_{trans} = 6.45$ Hz, $^3J_{trans} = 4.69$ Hz, 1H, 1-H), 7.27–7.31 (m, 3H, Ph), 7.35–7.42 (m, 2H, Ph), 8.01 (s, 1H, N*H*H), 8.37 (s, 1H, NH*H*).

– ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.2 (C-2), 19.5 (C-3), 43.0 (C-1), 79.2 (*C*≡C–Ph), 88.7 (C≡*C*–Ph), 122.7 (*ipso*-C), 128.2 (*p*-C), 128.3 (*m*-C), 131.7 (*o*-C), 217.2 (*cis*-C=O), 222.9 (*trans*-C=O), 287.8 (Cr=C). – MS (70 eV), *m/z* (%): 361 (20) [M^+], 305 (2) [M^+ – 2 CO], 277 (14) [M^+ – 3 CO], 249 (60) [M^+ – 4 CO], 221 (100) [M^+ – 5 CO], 169 (19) [M^+ – $Cr(CO)_5$], 80 (20), 52 (45) [Cr^+]. – HR-MS: calcd. 361.0042; found 361.0037. – $C_{17}H_{11}CrNO_5$ (361.27): calcd. C 56.52, H 3.07, N 3.88; found C 56.35, H 3.13, N 4.00.

[Amino(trans-2-phenylethynylcyclopropyl)methylidene]pentacarbonyltungsten(0) (**10**): Yield 2.32 g (94%), R_f = 0.38 (PE/CH_2Cl_2, 1:1). – IR (hexane): ṽ [ν(C=O)] = 2066 cm^{-1} (m, A_1), 1969 (w, B_1), 1944 (vs, E), 1921 (s, A_1). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.62 (ddd, $^3J_{cis}$ = 9.00 Hz, $^3J_{trans}$ = 6.06 Hz, ^2J = 5.08 Hz, 1H, 3-H), 1.67 (ddd, $^3J_{cis}$ = 8.41 Hz, $^3J_{trans}$ = 6.45 Hz, ^2J = 5.08 Hz, 1H, 3-H), 2.16 (ddd, $^3J_{cis}$ = 9.00 Hz, $^3J_{trans}$ = 6.45 Hz, $^3J_{trans}$ = 4.50 Hz, 1H, 2-H), 2.55 (ddd, $^3J_{cis}$ = 8.41 Hz, $^3J_{trans}$ = 6.06 Hz, $^3J_{trans}$ = 4.50 Hz, 1H, 1-H), 7.28–7.33 (m, 3H, Ph), 7.35–7.41 (m, 2H, Ph), 8.25 (s, 1H, N*H*H), 8.53 (s, 1H, NH*H*). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.1 (C-2), 20.7 (C-3), 45.1 (C-1), 79.2 (*C*≡C–Ph), 88.7 (C≡*C*–Ph), 122.7 (*ipso*-C), 128.2 (*p*-C), 128.3 (*m*-C), 131.6 (*o*-C), 197.9 (s, d, $^1J_{CW}$ = 127.6 Hz, *cis*-C=O), 202.5 (s, d, $^1J_{CW}$ = 129.0 Hz, *trans*-C=O), 264.9 (s, d, $^1J_{CW}$ = 94.3 Hz, W=C). – MS (70 eV), *m/z* (rel. ^{184}W %): 493 (10) [M^+], 465 (2) [M^+ – CO], 437 (20) [M^+ – 2 CO], 409 (8) [M^+ – 3 CO], 381 (55) [M^+ – 4 CO], 353 (98) [M^+ – 5 CO], 351 (100), 325 (32), 128 (12). – HR-MS (^{182}W): calcd. 491.0120; found 491.0133. – $C_{17}H_{11}NO_5W$ (493.12): calcd. C 41.41, H 2.25, N 2.84; found C 41.38, H 2.42, N 2.91.

General Procedure for the Preparation of Hexacarbonyldicobalt Complexes **2c**, **2t**, **11**, **12**: At 0 °C 2.22 g (6.5 mmol) of dicobaltoctacarbonyl was added to a solution of 5 mmol alkyne (**1c**, **1t**, **9** or **10**) in 100 ml dichloromethane. The mixture was allowed to warm to room temp. and stirred for 2 h. The solvent was removed in vacuo and chromatography [0 °C, silica gel, petroleum ether/dichloromethane, 3:1 (esters); 1:1 (carbene complexes)] yielded dark-red to black oils or solids.

Hexacarbonyl-μ-η-(ethyl-cis-2-phenylethynylcyclopropanecarboxylate)dicobalt (Co–Co) (**2c**): Yield 2.38 g (95%), R_f = 0.19 (PE/CH_2Cl_2, 3:1), dark-red oil. – IR (hexane): ṽ [ν(C=O)] = 2093 cm^{-1} (m), 2054 (vs), 2035 (m), 2023 (s), 2009 (w). – ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.15 (t, $^3J_{HH}$ = 7.15 Hz, 3H, CH_3), 1.68 (m_c, 2H, *c*-C_3H_4), 2.25 (m_c, 1H, *c*-C_3H_4), 2.75 (m_c, 1H, *c*-C_3H_4), 3.95 (q, $^3J_{HH}$ = 7.15 Hz, 2H, O-CH_2), 7.25–7.36 (m, 3H, Ph), 7.46–7.51 (m, 2H, Ph). – ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.0 (q, $^1J_{CH}$ = 127.2 Hz, CH_3), 18.5 (t, $^1J_{CH}$ = 165.0 Hz, C-3), 24.9 (d, $^1J_{CH}$ = 167.0 Hz, *c*-C_3H_4), 25.0 (d, $^1J_{CH}$ = 165.5 Hz, *c*-C_3H_4), 60.8 (tq, $^1J_{CH}$ = 147.8 Hz, $^2J_{CH}$ = 4.3 Hz, CH_2), 92.9 (s, *C*≡C-Ph), 94.6 (s, C≡*C*-Ph), 127.4 (dt, $^1J_{CH}$ = 161.2 Hz, $^3J_{CH}$ = 7.4 Hz, *o*-C), 128.6 (dd, $^1J_{CH}$ = 154.5 Hz, $^3J_{CH}$ = 6.7 Hz, *p*-C), 129.2 (d, $^1J_{CH}$ = 161.3 Hz, *m*-C), 138.5 (t, $^3J_{CH}$ = 7.9 Hz, *ipso*-C), 170.2 (s, C=O), 199.4 (s, br, Co-C=O). – MS (70 eV), *m/z* (%): 472 (1) [M^+ – CO], 444 (9) [M^+ – 2 CO], 416 (6) [M^+ – 3 CO], 388 (8) [M^+ – 4 CO], 360 (43) [M^+ – 5 CO], 332 (9) [M^+ – 6 CO], 214 (56) [M^+ – $Co_2(CO)_6$], 169 (15) [M^+ – $Co_2(CO)_6$ – OC_2H_5], 141 (100) [M^+ – $Co_2(CO)_6$ – $COOC_2H_5$], 115 (39) [$C_9H_7^+$], 77 (7) [$C_6H_5^+$]. – $C_{20}H_{14}Co_2O_8$ (500.19): calcd. C 48.03, H 2.82; found C 48.00, H 2.95.

Hexacarbonyl-μ-η-(ethyl-trans-2-phenylethynylcyclopropanecarboxylate)dicobalt (Co–Co) (**2t**): Yield 2.28 g (91%), R_f = 0.33 (PE/CH_2Cl_2, 3:1), dark-red oil. – IR (hexane): ṽ [ν(C=O)] = 2091 cm^{-1} (m), 2056 (vs), 2029 (s), 2014 (w). – ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.27 (t, $^3J_{HH}$ = 7.08 Hz, 3H, CH_3), 1.28 (ddd, $^3J_{cis}$ = 8.54 Hz, $^3J_{trans}$ = 6.10 Hz, $^2J_{HH}$ = 4.40 Hz, 1H, 3-H), 1.83 (ddd, $^3J_{cis}$ = 8.79 Hz, $^3J_{trans}$ = 5.37 Hz, $^2J_{HH}$ = 4.40 Hz, 1H, 3-H), 1.98 (ddd, $^3J_{cis}$ = 8.54 Hz, $^3J_{trans}$ = 5.37 Hz, $^3J_{trans}$ = 3.91 Hz, 1H, *c*-C_3H_4), 2.87 (ddd, $^3J_{cis}$ = 8.79 Hz, $^3J_{trans}$ = 6.10 Hz, $^3J_{trans}$ = 3.91 Hz, 1H, *c*-C_3H_4), 4.18 (q, $^3J_{HH}$ = 7.08 Hz, 2H, O-CH_2), 7.26–7.39 (m, 3H, Ph), 7.44–7.51 (m, 2H, Ph). – ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.2 (q, $^1J_{CH}$ = 126.2 Hz, CH_3), 20.5 (t, $^1J_{CH}$ = 165.8 Hz, C-3), 25.5 (d, $^1J_{CH}$ = 169.2 Hz, *c*-C_3H_4), 26.7 (d, $^1J_{CH}$ = 170.6 Hz, *c*-C_3H_4), 60.9 (t, $^1J_{CH}$ = 147.0 Hz, CH_2), 91.3 (s, *C*≡C-Ph), 99.1 (s, C≡*C*-Ph), 127.9 (dt, $^1J_{CH}$ = 161.6 Hz, $^3J_{CH}$ = 8.1 Hz, *o*-C), 128.9 (dd, $^1J_{CH}$ = 160.9 Hz, $^3J_{CH}$ = 8.3 Hz, *p*-C), 129.1 (dt, $^1J_{CH}$ = 160.5 Hz, $^3J_{CH}$ = 6.9 Hz, *m*-C), 137.7 (t, $^3J_{CH}$ = 7.6 Hz, *ipso*-C), 172.4 (s, C=O), 199.1 (s, br, Co-C=O). – MS (70 eV), *m/z* (%): 472 (0.3) [M^+ – CO], 444 (13) [M^+ – 2 CO], 416 (8) [M^+ – 3 CO], 388 (12) [M^+ – 4 CO], 360 (47) [M^+ – 5 CO], 332 (10) [M^+ – 6 CO], 214 (56) [M^+ – $Co_2(CO)_6$], 169 (18) [M^+ – $Co_2(CO)_6$ – OC_2H_5], 141 (100) [M^+ – $Co_2(CO)_6$ – $COOC_2H_5$], 115 (40) [$C_9H_7^+$], 77 (6) [$C_6H_5^+$]. – $C_{20}H_{14}Co_2O_8$ (500.19): calcd. C 48.03, H 2.82; found C 47.96, H 3.04.

Hexacarbonyl-μ-η-{[amino(trans-2-phenylethynylcyclopropyl)methylidene]pentacarbonylchromium(0)}dicobalt (Co–Co) (**11**): Yield 2.78 g (86%), R_f = 0.47 (PE/CH_2Cl_2, 1:1), black solid. – IR (hexane): ṽ [ν(C=O)] = 2093 cm^{-1} (m), 2058 (vs), 2033 (br, s), 1969 (w, B_1), 1946 (vs, E), 1921 (s, A_1). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.68 (dt, $^3J_{cis}$ = 8.90 Hz, J = 5.58 Hz, 1H, 3-H), 1.96 (dt, $^3J_{cis}$ = 8.75 Hz, J = 5.84 Hz, 1H, 3-H), 2.91 (ddd, $^3J_{cis}$ = 8.90 Hz, $^3J_{trans}$ = 5.48 Hz, $^3J_{trans}$ = 4.50 Hz, 1H, 2-H), 3.06 (ddd, $^3J_{cis}$ = 8.75 Hz, $^3J_{trans}$ = 6.26 Hz, $^3J_{trans}$ = 4.50 Hz, 1H, 1-H), 7.31–7.39 (m, 3H, Ph), 7.44–7.52 (m, 2H, Ph), 8.05 (s, 1H, N*H*H), 8.38 (s, 1H, NH*H*). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.2 (C-2), 29.3 (C-3), 46.3 (C-1), 91.6 (*C*≡C-Ph), 97.7 (C≡*C*-Ph), 128.2 (*p*-C), 129.0 (*o*-C), 129.1 (*m*-C), 137.5 (*ipso*-C), 199.0 (br, Co-C=O), 217.3 (*cis*-C=O), 222.4 (*trans*-C=O), 289.0 (Cr=C). – MS (70 eV), *m/z* (%): 646.7 (4) [M^+], 338.8 (9) [M^+ – 11 CO], 219.9 (43), 169.1 (76), 79.9 (93), 52 (100) [Cr^+]. – $C_{23}H_{11}CrCo_2NO_{11}$ (647.2): calcd. C 42.68, H 1.71, N 2.16; found C 42.60, H 1.77, N 2.29.

Hexacarbonyl-μ-η-{[amino(trans-2-phenylethynylcyclopropyl)methylidene]pentacarbonyltungsten(0)}dicobalt (Co–Co) (**12**): Yield 3.27 g (84%), R_f = 0.51 (PE/CH_2Cl_2, 1:1), black solid. – IR (hexane): ṽ [ν(C=O)] = 2093 cm^{-1} (m), 2066 (m, A_1), 2058 (s), 2033 (br, s), 2026 (s), 1969 (w, B_1), 1944 (vs, E), 1917 (s, A_1). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.66 (ddd, $^3J_{cis}$ = 8.61 Hz, $^3J_{trans}$ = 6.26 Hz, $^2J_{HH}$ = 5.28 Hz, 1H, 3-H), 2.09 (ddd, $^3J_{cis}$ = 8.83 Hz, $^3J_{trans}$ = 5.48 Hz, $^2J_{HH}$ = 5.28 Hz, 1H, 3-H), 2.39 (ddd, $^3J_{cis}$ = 8.61 Hz, $^3J_{trans}$ = 5.48 Hz, $^3J_{trans}$ = 4.11 Hz, 1H, 2-H), 3.13 (ddd, $^3J_{cis}$ = 8.83 Hz, $^3J_{trans}$ = 6.26 Hz, $^3J_{trans}$ = 4.11 Hz, 1H, 1-H), 7.28–7.38 (m, 3H, Ph), 7.42–7.52 (m, 2H, Ph), 8.23 (s, 1H, N*H*H), 8.49 (s, 1H, NH*H*). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.9 (C-2), 30.8 (C-3), 48.4 (C-1), 91.5 (*C*≡C-Ph), 97.7 (C≡*C*-Ph), 128.2 (*p*-C), 129.0 (*o*-C), 129.1 (*m*-C), 137.4 (*ipso*-C), 198.1 (s, d, $^1J_{CW}$ = 127.6 Hz, *cis*-C=O], 199.0 (br, Co-C=O), 202.1 (s, d, $^1J_{CW}$ = 126.2 Hz, *trans*-C=O), 289.0 (s, d, $^1J_{CW}$ = 90.2 Hz, C=W). – MS (70 eV), *m/z* (rel. ^{184}W %): 779 (<1) [M^+], 469 (11) [M^+ – 11 CO], 351 (27), 268 (35), 169.1 (100). – $C_{23}H_{11}Co_2NO_{11}W$ (779.1): calcd. C 35.46, H 1.42, N 1.80; found C 35.73, H 1.59, N 1.93.

General Procedure for the Pauson-Khand Reaction of Cobalt Functionalized Alkynes with Norbornene: A solution of 5 mmol cobalt complex (**2c**, **2t** or **11**) and 2.35 g (25 mmol) norbornene in 150 ml toluene was warmed to 90 °C (for reaction times see Table

1). After cooling to room temp. the solution was filtered through silica gel and the solvent was removed in vacuo. The brown-violet residue was then submitted to column chromatography (silica gel). After the excess norbornene and cobalt carbonyls had been removed with petroleum ether, elution with dichloromethane yielded a band containing all four tricyclodecenone isomers. A second chromatographic separation (esters: silica gel, petroleum ether/diethyl ether, 2:1; carbene complexes: −5°C, silica gel, petroleum ether/ethyl acetate, 3:1) was used to separate the four isomers into pairs of diastereomers. The given R_f values refer to the second chromatography. Compounds **3** and **4** were separated by fractional crystallization from hexane, and compounds **15** and **16** were separated by fractional crystallization from hexane/dichloromethane.

Table 1

Cobalt complex	Reaction time	Products
2t	66 h	**3–6**
2c	144 h	poor yield
11	24 h	**13–16**

(1RS,2RS,2'SR,6'RS)-Ethyl trans-2-(5-Oxo-3-phenyl-tricyclo[5.2.1.0^{2,6}]dec-3-ene-4-yl)cyclopropanecarboxylate (**3**): Yield 0.17 g (10%), R_f = 0.30 (PE/Et_2O), colourless crystals, m.p. 120−121°C (hexane). − IR (film): $\tilde{\nu}$ = 1722 cm^{-1} (C=O), 1688 (C=O). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.90 (d, $^2J_{HH}$ = 10.46 Hz, 1H, 10'-H), 1.02 (d, $^2J_{HH}$ = 10.46 Hz, 1H, 10'-H), 1.18 (t, $^3J_{HH}$ = 7.14 Hz, 3H, CH_3), 1.29 (m, 2H, CH_2), 1.40 (ddd, $^3J_{cis}$ = 9.60 Hz, $^3J_{trans}$ = 5.10 Hz, $^2J_{HH}$ = 3.70 Hz, 1H, 3-H), 1.54 (ddd, $^3J_{cis}$ = 8.40 Hz, $^3J_{trans}$ = 6.80 Hz, $^2J_{HH}$ = 3.70 Hz, 1H, 3-H), 1.57 (m, 2H, CH_2), 1.95 (s, br, 1H, CH), 2.19 (ddd, $^3J_{cis}$ = 9.60 Hz, $^3J_{trans}$ = 6.80 Hz, $^3J_{trans}$ = 4.50 Hz, 1H, 1-H), 2.25 (d, br, $^3J_{HH}$ = 5.30 Hz, 1H, 2'-H), 2.41 (s, br, 1H, CH), 2.47 (ddd, $^3J_{cis}$ = 8.40 Hz, $^3J_{trans}$ = 5.10 Hz, $^3J_{trans}$ = 4.50 Hz, 1H, 2-H), 2.95 (d, br, $^3J_{HH}$ = 5.30 Hz, 1H, 6'-H), 4.03 (q, $^3J_{HH}$ = 7.14 Hz, 2H, O-CH_2), 7.36−7.47 (m, 5H, Ph). − ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.21 (qt, $^1J_{CH}$ = 126.7 Hz, $^2J_{CH}$ = 2.7 Hz, CH_3), 14.79 (t, $^1J_{CH}$ = 165.4 Hz, C-3), 19.07 (d, $^1J_{CH}$ = 165.6 Hz, C-1), 19.18 (d, $^1J_{CH}$ = 171.8 Hz, C-2), 28.71 (t, $^1J_{CH}$ = 129.7 Hz, CH_2), 28.88 (t, $^1J_{CH}$ = 131.7 Hz, CH_2), 31.35 (t, $^1J_{CH}$ = 133.4 Hz, C-10'), 38.04 (d, $^1J_{CH}$ = 141.8 Hz, C-1'), 39.16 (d, $^1J_{CH}$ = 142.3 Hz, C-7'), 50.60 (d, $^1J_{CH}$ = 140.1 Hz, C-2'), 54.09 (d, $^1J_{CH}$ = 138.6 Hz, C-6'), 60.51 (t, $^1J_{CH}$ = 147.2 Hz, O-CH_2), 127.94 (dt, $^1J_{CH}$ = 159.7 Hz, $^3J_{CH}$ = 6.7 Hz, *p*-C), 128.66 (d, $^1J_{CH}$ = 161.0 Hz, *o*-C), 129.41 (dt, $^1J_{CH}$ = 161.7 Hz, $^3J_{CH}$ = 6.9 Hz, *m*-C), 135.22 (t, $^3J_{CH}$ = 6.9 Hz, *ipso*-C), 139.17 (s, α-C=C), 171.70 (s, β-C=C), 174.06 (s, COOEt), 209.35 (s, C=O). − MS (70 eV), *m/z* (%): 336.3 (27) [M$^+$], 290.2 (15) [M$^+$ − C_2H_6O], 262.3 (100), 195.2 (20), 165.1 (30), 115.0 (25) [$C_9H_7^+$], 91.0 (20) [$C_7H_7^+$], 67.1 (32) [$C_4H_3O^+$]. − HR-MS: calcd. 336.1725; found 336.1732. − $C_{22}H_{24}O_3$ (336.4): calcd. C 78.54, H 7.19; found C 78.49, H 6.87.

(1RS,2RS,2'RS,6'SR)-Ethyl trans-2-(5-Oxo-3-phenyl-tricyclo[5.2.1.0^{2,6}]dec-3-ene-4-yl)cyclopropanecarboxylate (**4**): Yield 0.13 g (8%), R_f = 0.30 (PE/Et_2O), colourless solid. − IR (film): $\tilde{\nu}$ = 1722 cm^{-1} (C=O), 1688 (C=O). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.90 (d, $^2J_{HH}$ = 10.46 Hz, 1H, 10'-H), 1.02 (d, $^2J_{HH}$ = 10.46 Hz, 1H, 10'-H), 1.26 (t, $^3J_{HH}$ = 7.15 Hz, 3H, CH_3), 1.29 (m, 2H, CH_2), 1.40 (ddd, $^3J_{cis}$ = 9.60 Hz, $^3J_{trans}$ = 5.10 Hz, $^2J_{HH}$ = 3.80 Hz, 1H, 3-H), 1.73 (ddd, $^3J_{cis}$ = 8.40 Hz, $^3J_{trans}$ = 6.80 Hz, $^2J_{HH}$ = 3.80 Hz, 1H, 3-H), 1.57 (m, 2H, CH_2), 1.95 (s, br, 1H, CH), 2.19 (ddd, $^3J_{cis}$ = 9.60 Hz, $^3J_{trans}$ = 6.80 Hz, $^3J_{trans}$ = 4.50 Hz, 1H, 1-H), 2.25 (d, br, $^3J_{HH}$ = 5.30 Hz, 1H, 2'-H), 2.41 (s, br, 1H, CH), 2.47 (ddd, $^3J_{cis}$ = 8.40 Hz, $^3J_{trans}$ = 5.10 Hz, $^3J_{trans}$ = 4.50 Hz, 1H, 2-H), 2.95 (d, br, $^3J_{HH}$ = 5.30 Hz, 1H, 6'-H), 4.14 ($^3J_{HH}$ = 7.15 Hz, 2H, O-CH_2), 7.36−7.47 (m, 5H, Ph). − ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.61 (t, $^1J_{CH}$ = 165.4 Hz, C-3), 14.28 (qt, $^1J_{CH}$ = 128.4 Hz, $^2J_{CH}$ = 2.7 Hz, CH_3), 19.03 (d, $^1J_{CH}$ = 163.0 Hz, C-1), 20.89 (d, $^1J_{CH}$ = 169.1 Hz, C-2), 28.67 8t, $^1J_{CH}$ = 129.7 Hz, CH_2), 28.87 (t, $^1J_{CH}$ = 132.2 Hz, CH_2), 31.36 (t, $^1J_{CH}$ = 133.4 Hz, C-10'), 38.00 (d, $^1J_{CH}$ = 141.8 Hz, C-1'), 39.16 (d, $^1J_{CH}$ = 142.3 Hz, C-7'), 50.55 (d, $^1J_{CH}$ = 140.1 Hz, C-2'), 54.05 (d, $^1J_{CH}$ = 138.6 Hz, C-6'), 60.54 (t, $^1J_{CH}$ = 147.2 Hz, O-CH_2), 127.94 (dt, $^1J_{CH}$ = 159.7 Hz, $^3J_{CH}$ = 6.7 Hz, *p*-C), 128.56 (d, $^1J_{CH}$ = 161.0 Hz, *o*-C), 129.36 (dt, $^1J_{CH}$ = 161.7 Hz, $^3J_{CH}$ = 6.9 Hz, *m*-C), 135.17 (t, $^3J_{CH}$ = 6.9 Hz, *ipso*-C), 139.18 (s, α-C=C), 171.64 (s, β-C=C), 174.00 (s, COOEt), 209.28 (s, C=O). − MS (70 eV), *m/z* (%): 336.3 (27) [M$^+$], 290.2 (15) [M$^+$ − C_2H_6O], 262.3 (100), 195.2 (20), 165.1 (30), 115.0 (25) [$C_9H_7^+$], 91.0 (20) [$C_7H_7^+$], 67.1 (32) [$C_4H_3O^+$]. − HR-MS: calcd. 336.1725; found 336.1732. − $C_{22}H_{24}O_3$ (336.4): calcd. C 78.54, H 7.19; found C 78.49, H 6.87.

Ethyl trans-2-(5-Oxo-4-phenyl-tricyclo[5.2.1.0^{2,6}]dec-3-ene-3-yl)-cyclopropanecarboxylate (**5/6**): Yield 0.94 g (56%), R_f = 0.25 (PE/Et_2O, 2:1), colourless solid. − IR (film): $\tilde{\nu}$ = 1726 cm^{-1} (C=O), 1695 (C=O). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.02 (d, $^2J_{HH}$ = 10.46 Hz, 2H, 2 × 10'-H), 1.16 (d, $^2J_{HH}$ = 10.46 Hz, 2H, 2 × 10'-H), 1.25 (t, $^3J_{HH}$ = 7.20 Hz, 3H, CH_3), 1.26 (t, $^3J_{HH}$ = 7.20 Hz, 3H, CH_3), 1.30 (m, 4H, 2 × CH_2), 1.43 (ddd, $^3J_{cis}$ = 8.55 Hz, $^3J_{trans}$ = 6.85 Hz, J_{HH} = 4.65 Hz, 1H, *c*-C_3H_4), 1.5−1.78 (m, 7H, 2 × CH_2, 3 × *c*-C_3H_4), 2.00 (ddd, $^3J_{cis}$ = 8.50 Hz, $^3J_{trans}$ = 5.50 Hz, J_{HH} = 4.40 Hz, 1H, *c*-C_3H_4), 2.16 (ddd, $^3J_{cis}$ = 8.50 Hz, $^3J_{trans}$ = 5.30 Hz, J_{HH} = 4.70 Hz, 1H, *c*-C_3H_4), 2.28 (s, br, 2H, 2 × 2'-H), 2.30−2.48 (m, 6H, 4 × CH, 2 × *c*-C_3H_4), 2.50 (s, br, 2 × 6'-H), 4.14 (q, $^3J_{HH}$ = 7.20 Hz, 2H, O-CH_2), 4.15 (q, $^3J_{HH}$ = 7.20 Hz, 2H, O-CH_2), 7.25−7.41 (m, 10H, 2 × Ph). − ^{13}C NMR (125 MHz, $CDCl_3$, *major diastereomer*): δ = 14.12 (CH_3), 15.75 (C-3), 22.88 (C-1), 23.41 (C-2), 28.06 (CH_2), 29.16 (CH_2), 31.20 (C-10'), 38.39 (C−H), 39.00 (C−H), 48.17 (C-2'), 53.94 (C-6'), 60.81 (O-CH_2), 127.72 (*p*-C), 128.03 (*o*-C), 128.93 (*m*-C), 131.09 (*ipso*-C), 144.77 (α-C=C), 171.08 (β-C=C), 172.09 (COOEt), 207.78 (C=O). − ^{13}C NMR (125 MHz, $CDCl_3$, *minor diastereomer*): δ = 14.10 (CH_3), 15.83 (C-3), 22.67 (C-1), 23.30 (C-2), 28.04 (CH_2), 29.23 (CH_2), 31.23 (C-10'), 38.46 (C−H), 38.95 (C−H), 48.34 (C-2'), 54.03 (C-6'), 60.86 (O-CH_2), 127.74 (*p*-C), 128.05 (*o*-C), 128.99 (*m*-C), 131.11 (*ipso*-C), 144.62 (α-C=C), 171.16 (β-C=C), 172.11 (COOEt), 207.81 (C=O). − MS (70 eV), *m/z* (%): 336.3 (30) [M$^+$], 290.2 (15) [M$^+$ − C_2H_6O], 262.3 (100), 195.2 (17), 165.1 (23), 115.0 (18) [$C_9H_7^+$], 91.0 (15) [$C_7H_7^+$], 67.1 (20) [$C_4H_3O^+$]. − HR-MS: calcd. 336.1725; found 336.1723. − $C_{22}H_{24}O_3$ (336.4): calcd. C 78.54, H 7.19; found C 78.54, H 6.85.

{Amino[trans-2-(5-oxo-3-phenyl-tricyclo[5.2.1.0^{2,6}]dec-3-ene-4-yl)-cyclopropyl]methylidene}pentacarbonylchromium(0) (**13/14**): Yield 0.22 g (9%), R_f = 0.24 (PE/ethyl acetate, 3:1), yellow solid. − IR (hexane): $\tilde{\nu}$ [ν(C=O)] = 2056 cm^{-1} (m, A_1), 1940 (vs, E), 1926 (s, A_1). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.92 (m, 2H, 2 × 10'-H), 1.05 (m, 2H, 2 × 10'-H), 1.31 (d, br, J_{HH} = 9.30 Hz, 4H, 2 × CH_2), 1.39 (m, 1H, 3-H), 1.55 (m, 1H, 3-H), 1.60 (d, br, J_{HH} = 9.30 Hz, 4H, 2 × CH_2), 1.70 (m, 1H, 3-H), 1.83 (m, 1H, 3-H), 1.94 (m, 1H, 2-H), 1.97 (s, br, 1H, CH), 2.03 (s, br, 1H, CH), 2.11 (m, 1H, 2-H), 2.29 (s, br, 2H, 2 × CH), 2.44 (s, br, 2H, 2 × CH), 2.87 (m$_c$, 1H, 1-H), 2.95 (d, br, $^3J_{HH}$ = 5.10 Hz, 1H, CH), 3.02 (d, br, $^3J_{HH}$ = 5.10 Hz, 1H, CH), 3.26 (m$_c$, 1H, 1-H), 7.37−7.48 (m, 10H, Ph), 8.28 (s, br, 2H, NHH), 8.53 (s, br, 1H, NHH), 8.88 (s, br, 1H, NHH). − ^{13}C NMR (125 MHz, $CDCl_3$, *major diastereomer*): δ = 16.01 (C-3), 22.11 (C-2), 28.78 (CH_2), 28.86 (CH_2), 31.28 (C-10'), 38.06 (C-1'), 39.06 (C-7'), 41.72 (C-1), 50.71 (C-2'), 54.10 (C-6'), 128.11 (*o*-C), 128.68 (*m*-C), 129.86 (*p*-C), 134.42 (*ipso*-C), 138.98 (α-C=C), 172.00 (β-C=C), 210.52 (C=O), 217.52 (*cis*-C=O), 222.85 (*trans*-C=O), 289.74 (Cr=C). − ^{13}C

NMR (125 MHz, $CDCl_3$, *minor diastereomer*): δ = 17.19 (C-3), 22.27 (C-2), 28.59 (CH_2), 28.92 (CH_2), 31.34 (C-10′), 38.05 (C-1′), 39.15 (C-7′), 40.35 (C-1), 50.04 (C-2′), 54.14 (C-6′), 127.72 (*o*-C), 128.72 (*m*-C), 129.57 (*p*-C), 135.09 (*ipso*-C), 138.74 (α-C=C), 172.61 (β-C=C), 209.78 (C=O), 217.40 (*cis*-C=O), 222.66 (*trans*-C=O), 289.06 (Cr=C). – MS (70 eV), *m/z* (%): 483.1 (0.15) [M^+], 399.1 (0.15) [M^+ – 3 CO], 371 (0.27) [M^+ – 4 CO], 343.1 (6) [M^+ – 5 CO], 291.3 (100) [M^+ – $Cr(CO)_5$], 225.2 (45), 93.1 (52) [$C_7H_9^+$], 52.0 (45) [Cr^+]. – HR-MS: calcd. 343.1029; found 343.1042 for [M^+ – 5 CO]; calcd. 291.1623; found 291.1614 for [M^+ – $Cr(CO)_5$].

(1RS,2RS,2′RS,6′SR)-{Amino[trans-2-(5-oxo-4-phenyltricyclo[5.2.1.0^{2,6}]dec-3-ene-3-yl)cyclopropyl]methylidene}-pentacarbonylchromium(0) (**15**): Yield 0.34 g (14%), R_f = 0.16 (PE/ethyl acetate), yellow crystals, m.p. 105°C (hexane/dichloromethane). – IR (hexane): ṽ [ν(C=O)] = 2056 cm^{-1} (m, A_1), 1940 (vs, E), 1926 (s, A_1). – ^1H NMR (400 MHz, $CDCl_3$): δ = 1.04 (d, $^2J_{HH}$ = 10.56 Hz, 1H, 10′-H), 1.16 (d, $^2J_{HH}$ = 10.56 Hz, 1H, 10′-H), 1.35 (m_c, 2H, CH_2), 1.57–1.67 (m_c, 2H, CH_2), 1.70 (m_c, 1H, 3-H), 1.81 (m_c, 1H, 3-H), 2.29 (m_c, br, 1H, CH), 2.36 (d, $^3J_{HH}$ = 5.10 Hz, 1H, CH), 2.47 (d, $^3J_{HH}$ = 5.10 Hz, 1H, CH), 2.48 (m, superimposed, 1H, 2-H), 2.51 (m_c, br, 1H, CH), 2.97 (ddd, $^3J_{cis}$ = 8.40 Hz, $^3J_{trans}$ = 5.90 Hz, $^3J_{trans}$ = 4.90 Hz, 1H, 1-H), 7.18–7.23 (m, 2H, Ph), 7.28–7.41 (m, 3H, Ph), 7.85 (s, br, 1H, N*H*H), 8.25 (s, br, 1H, NH*H*). – ^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.24 (t, $^1J_{CH}$ = 164.3 Hz, C-3), 27.78 (d, $^1J_{CH}$ = 163.2 Hz, C-2), 28.09 (t, $^1J_{CH}$ = 131.5 Hz, CH_2), 29.28 (t, $^1J_{CH}$ = 135.3 Hz, CH_2), 31.39 (t, $^1J_{CH}$ = 133.4 Hz, C-10′), 38.63 (d, $^1J_{CH}$ = 142.1 Hz, C-1′), 39.08 (d, $^1J_{CH}$ = 144.9 Hz, C-7′), 41.71 (d, $^1J_{CH}$ = 167.5 Hz, C-1), 48.13 (d, $^1J_{CH}$ = 137.7 Hz, C-2′), 54.23 (d, $^1J_{CH}$ = 138.7 Hz, C-6′), 128.25 (d, $^1J_{CH}$ = 161.6 Hz, *p*-C), 128.53 (d, $^1J_{CH}$ = 162.2 Hz, *o*-C), 129.08 (d, $^1J_{CH}$ = 158.3 Hz, *m*-C), 131.26 (s, *ipso*-C), 144.95 (s, α-C=C), 171.77 (s, β-C=C), 208.77 (s, C=O), 217.31 (s, *cis*-C=O), 222.50 (s, *trans*-C=O), 286.04 (s, Cr=C). – MS (70 eV), *m/z* (%): 483.1 (0.15) [M^+], 399.1 (0.15) [M^+ – 3 CO], 371 (0.27) [M^+ – 4 CO], 343.1 (6) [M^+ – 5 CO], 291.3 (100) [M^+ – $Cr(CO)_5$], 225.2 (45), 93.1 (52) [$C_7H_9^+$], 52.0 (45) [Cr^+]. – HR-MS: calcd. 371.0978; found 371.0978 for [M^+ – 4 CO]; calcd. 343.1029; found 343.1022 for [M^+ – 5 CO]. – $C_{25}H_{21}CrO_6N \cdot 1/2\ CH_2Cl_2$ (525.9): calcd. C 58.28, H 4.22, N 2.67; found C 58.27, H 4.56, N 2.28.

(1SR,2SR,2′RS,6′SR)-{Amino[trans-2-(5-oxo-4-phenyl-tricyclo[5.2.1.0^{2,6}]dec-3-ene-3-yl)cyclopropyl]methylidene}-pentacarbonylchromium(0) (**16**): Yield 0.22 g (9%), R_f = 0.16 (PE/ethyl acetate), yellow solid. – IR (hexane): ṽ [ν(C=O)] = 2056 cm^{-1} (m, A_1), 1940 (vs, E), 1926 (s, A_1). – ^1H NMR (500 MHz, $CDCl_3$): δ = 1.05 (d, $^2J_{HH}$ = 10.48 Hz, 1H, 10′-H), 1.13 (d, $^2J_{HH}$ = 10.48 Hz, 1H, 10′-H), 1.33 (m_c, 2H, CH_2), 1.53 (m_c, 1H, 3-H), 1.59 (m_c, 2H, CH_2), 1.62 (m_c, 1H, 3-H), 2.26 (s, br, 1H, CH), 2.34 (m_c, 1H, 2-H), 2.37 (s, br, 1H, CH), 2.41 (s, br, 1H, CH), 2.44 (s, br, 1H, CH), 3.22 (m_c, 1H, 1-H), 7.16–7.20 (m, 2H, Ph), 7.26–7.34 (m, 3H, Ph), 8.11 (s, br, 1H, N*H*H), 8.18 (s, br, 1H, NH*H*). – ^{13}C NMR (125 MHz, $CDCl_3$): δ = 18.79 (t, $^1J_{CH}$ = 164.3 Hz, C-3), 28.23 (t, $^1J_{CH}$ = 131.5 Hz, CH_2), 28.26 (d, $^1J_{CH}$ = 163.2 Hz, C-2), 29.34 (t, $^1J_{CH}$ = 135.3 Hz, CH_2), 31.34 (t, $^1J_{CH}$ = 133.4 Hz, C-10′), 38.63 (d, $^1J_{CH}$ = 142.1 Hz, C-1′), 39.08 (d, $^1J_{CH}$ = 144.9 Hz, C-7′), 41.24 (d, $^1J_{CH}$ = 167.5 Hz, C-1), 48.71 (d, $^1J_{CH}$ = 137.7 Hz, C-2′), 54.43 (d, $^1J_{CH}$ = 138.7 Hz, C-6′), 128.25 (d, $^1J_{CH}$ = 161.6 Hz, *p*-C), 128.51 (d, $^1J_{CH}$ = 162.2 Hz, *o*-C), 129.20 (d, $^1J_{CH}$ = 158.3 Hz, *m*-C), 131.31 (s, *ipso*-C), 144.81 (s, α-C=C), 171.89 (s, β-C=C), 208.88 (s, C=O), 217.41 (s, *cis*-C=O), 222.63 (s, *trans*-C=O), 286.34 (s, Cr=C). – MS (70 eV), *m/z* (%): 483.1 (0.15) [M^+], 399.1 (0.15) [M^+ – 3 CO], 371 (0.27) [M^+ – 4 CO], 343.1 (6) [M^+ – 5 CO], 291.3 (100) [M^+ – $Cr(CO)_5$], 225.2 (45), 93.1 (52) [$C_7H_9^+$], 52.0 (45) [Cr^+]. – HR-MS: calcd. 371.0978; found 371.0978 for [M^+ – 4 CO]; calcd. 343.1029; found 343.1022 for [M^+ – 5 CO].

X-ray Crystallographic Studies of **3** *and* **15**[11]: The structures were solved by direct methods. Nonhydrogen atoms were refined anisotropically. Hydrogen atoms were localized by difference electron density determination and refined using a riding model. In **3** an extinction correction was applied. In **15** the solvent was disordered. Details of data collection and refinement are given in Table 2. Programs used: SHELXTL-Plus, G. M. Sheldrick, Siemens Analytical X-ray Instruments, Inc., Madison, Wi., USA (1989); SHELXL-93, G. M. Sheldrick, University of Göttingen, Germany (1993).

Table 2. Crystallographic data and summary of data collection and refinement

Compound	**3**	**15**
formula	$C_{22}H_{24}O_3$	$C_{25}H_{21}CrNO_6 \cdot ½\ CH_2Cl_2$
M	336.4	525.9
colour	colourless	yellow
crystal dimensions [mm]	0.45 × 0.40 × 0.20	0.65 × 0.55 × 0.40
crystal system	monoclinic	triclinic
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
a [pm]	1383.9(1)	1161.8(3)
b [pm]	992.2(1)	1358.3(3)
c [pm]	1321.1(1)	1820.2(4)
α [°]	90	102.00(2)
β [°]	95.97(1)	102.34(2)
γ [°]	90	93.40(2)
V [nm^3]	1.804(1)	2.729(1)
Z	4	4
$\rho_{calcd.}$ [g cm^{-3}]	1.24	1.28
μ [mm^{-1}]	0.64	0.55
F(000)	720	1084
full-matrix least-squares refinement on	F^2	F^2
parameter/restraints	228/0	631/10
measured reflections	2807	10619
unique reflections used in refinement	2668	9632
wR2	0.142	0.247
R1 [for $I > 2\sigma(I)$]	0.048	0.075
largest difference peak and hole [e nm^{-3} 10^3]	0.20/–0.17	0.82/–0.45
diffractometer	Enraf-Nonius CAD4	Nicolet R3m
radiation	Cu *Kα*	Mo *Kα*
monochromator	graphite	graphite
λ [pm]	154.178	71.073
T [K]	293(2)	293(2)
$2\Theta_{max.}$ [°]	120	50
	$-15 \le h \le 15$	$-13 \le h \le 13$
	$-11 \le k \le 0$	$-16 \le k \le 15$
	$-14 \le l \le 0$	$-1 \le l \le 21$

☆ Dedicated to Professor Dr. *G. E. Herberich* on the occasion of his 60th birthday.

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[11] Further details of the crystal structure investigations are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository numbers CSD-406363 (**3**) and CSD-406362 (**15**), the name of the authors and the publication.

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