Triaminocyclopentadienyl Ruthenium Complexes – New Catalysts for Cascade Conversions of Propargyl Alcohols

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Abstract: Various triaminocyclopentadienyl ruthenium complexes have been synthesized from Ru$_3$(CO)$_{12}$. The new complexes were tested for their ability to catalyze cascade conversions of propargyl alcohols. Their associated catalytic activities complement the activities of known diaminocyclopentadienone ruthenium complexes. In particular, the substrate scope of catalytic cycloadditions with 3-ketolactones or phloroglucinol derivatives is extended to terpenoid-derived propargyl alcohols containing an internal alkyne moiety. A wide range of cyclic terpenoid and phloroglucinol adducts are obtained by complementary application of both types of catalysts.

Introduction

Transition metal-catalyzed cascade reactions provide an atom-economical approach to the efficient synthesis of complex molecular scaffolds. Such transformations are particularly suitable for the preparation of natural products and analogues as important lead structures in the context of drug discovery.[1,2] With regard to the multiply functionalized precursors required for the desired cascade conversions, 1-alkenylpropargyl alcohols (1-en-4-yn-3-ols) are particularly noteworthy. These enynols are directly accessible from a broad range of readily available α,β-unsaturated aldehydes or ketones by acetylide addition. All carbon atoms of this versatile C_5 subunit are selectively addressable with the aid of various transition-metal catalysts. Due to the presence of three different functional groups, several modes of activation can be applied, giving rise to diverse cascade transformations.[3]

Ruthenium cyclopentadienone complexes of type I catalyze diverse cascade conversions of 1-alkenylpropargyl alcohols 2 with various nucleophiles.[4] An acidic promoter is beneficial in most cases. The redox-coupling between the metal and the ligand in complexes of type I is crucial for all of these conversions and the activation of the alkyne unit in 2 depends most likely on electrophilic ruthenium(II) species 1’ that is privileged under acidic conditions (Scheme 1). The mode of activation depends on the nature of the substrate. Terminal propargyl alcohols 2 (R¹ = H) are converted via alkynyl complex I, which is in equilibrium with the corresponding vinylidene compound II. Subsequent loss of water generates allenylidene species III. Secondary derivatives 2 (R¹, R² = H) are alternatively transformed in a redox-isomerization process to generate alkenyl species IV. Internal substrates 2 (R¹ ≠ H) are activated via π-complex V. Subsequent trapping of the metalated intermediates I–V with various nucleophiles give rise to diverse carbon- and heterocyclic compounds with release of the catalytically active species.[4] Thus, in presence of cyclic 1,3-dicarbonyl compounds, terminal secondary substrates 2 (R¹, R² = H) form...

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Michael-adducts 3 or spirocyclohexanones 4, whereas terminal tertiary substrates 2 \( (R^1 = H, R^2 \neq H) \) are converted to methylene spirocyclopentenes 5 in an allylation/carbocyclization cascade. Internal secondary substrates 2 \( (R^1 \neq H, R^2 = H) \) form 4H-pyrans 6 with cyclic 1,3-dicarbonyl compounds in a formal cycloaddition process (Scheme 1).

Exchange of the ligand's carbonyl oxygen for nitrogen should dramatically affect the redox-coupling with the metal and could thereby alter the catalyst's mode of action. Herein, we present various trimonocyclopentadienyl ruthenium(II) complexes of type 7 and compare some of their catalytic activities with the activity of diamino-cyclopentadienone catalyst 1a (Scheme 2). Complexes of type 7 can be regarded as aza analogues of the activated species 1'.

**Results and Discussion**

The ligands L7 are generated from cyclopentadienone L1a by a modified protocol of the method from Gompper et al.\[5\] Complexes 7 are formed from iminium precursors L7 as formal ruthenium(II) species, whereas catalysts of type 1 derived from cyclopentadienone precursors L1 arise as formal ruthenium(0) complexes (Scheme 2).\[4c,6\]

Various primary amines are suitable for this conversion including enantipure derivatives. The range of appropriate secondary amines, however, is rather limited due to strong steric repulsion in the planar iminium compounds L7. Further conversion of L7 with ruthenium carbonyl results in the formation of the desired trimonocyclopentadienyl complexes 7 in almost all cases. The highest yields are obtained from ligand L7j and complex 7j can be easily prepared in racemic or enantiopure (R)- or (S)-form from inexpensively commercially available amines. Therefore, complex 7j was used as an exemplary representative of the aza-catalysts 7. Broadening of the corresponding NMR-signals indicates a significant hindrance to the rotation of the phenyl groups in all complexes of type 7. Formation of complex 7o is not successful due to the metal chelating effect of the guanidine unit (Figure 1). We previously reported on the related synthesis of N-unsubstituted complex 7a.\[4c\]

Next, we compared some of the catalytic activities of the new catalysts 7 towards 1-alkenypropargyl alcohols 2 with those of catalyst 1a. We based the first systematic comparative study on the allylation/carbocyclization cascade of terminal tertiary 1-alkenypropargyl alcohols 2 with cyclic carbon nucleophiles. Conversion of alcohol 2a with 1,3-cyclohexanedione (A) in toluene (1.0 M) at 100 °C in presence of catalyst 1a (2 mol%) and trifluoroacetic acid (TFA, 4 mol%) as an acidic promoter, generates compound 5Aa in 82% yield (Scheme 3; Table 1, entry 3). No conversion was observed in absence of the...
catalyst and a significantly lower yield was obtained in absence of the acidic promoter (Table 1, entries 1, 2). At 170 °C (microwave irradiation) a significant lower yield is obtained (Table 1, entry 4). Complex 1a shows high long-term stability at higher temperature and no decomposition is observed at 170 °C in toluene about 20 h. However, in presence of the acidic promoter (2 equiv.), decomposition occurs at elevated temperatures. At 170 °C, 49% of 1a remained after 5 minutes, 34% after 10 minutes and 25% after 15 minutes (determined by NMR using an internal standard). Only small amounts of product 5Aa are obtained if Ru₄(CO)₁₉, [Ru(CO)₃Cl]₂ or the tetracyclone complex Tcc were applied as catalysts under similar reaction conditions (Table 1, entries 5–10). Exemplary aza-catalyst 7j was applied in absence of an acidic promoter, since a counterproductive effect has been observed (Table 1, entries 11–13). Unfortunately, only low yields of 5Aa are obtained at 100 °C, as well as at 170 °C, even though complex 7j shows no remarkable decomposition at 170 °C.

In contrast, if β-ketoactones like 4-hydroxycoumarin (B) are used as nucleophiles, catalysts of type 7 exhibit much higher activity. At a concentration of 1.0 M, full conversion of the substrates and comparably high yields of product 5Ba are obtained with catalyst 1a in presence of an acidic promoter at 100 °C (5 h) or at 170 °C (μW, 15 min) as well as with catalyst 7j in absence of an acidic promoter (Scheme 4; Table 2, entries 1, 2, 18). The reaction rate decreases with higher dilution. At a concentration of 0.25 M, 56% of the nucleophile B has been converted in presence of catalyst 1a (2 mol-%) and TFA (4 mol-%) after 15 minutes at 170 °C (Table 2, entries 2–4). The latter conditions are applied to compare the activities of all new complexes 7. Complex 7e exhibits the highest activity, but no improvement regarding the yield of 5Ba is observed at higher concentration. In contrast, full conversion is observed at a concentration of 1.0 M with less active complex 7j (Table 2, entries 10, 11, 18). Therefore, complex 7j represents a good compromise in terms of stability, activity, and availability.

Similar results are obtained with other substrates. In general, high yields of products 5 are obtained from alcohols 2a–d with 2-keto lactones if catalyst 1a with an acidic promoter or catalyst 7j are applied at 170 °C (μW, 15 min). With 1,3-diketones, however, high yields are only obtained with catalyst 1a and an acidic promoter at 100 °C (5 h). The yields and diastereoselectivities of the reactions catalyzed by complex 7j are generally lower, compared to the same reactions catalyzed by 1a (Scheme 5; Table 3; Figure 2).

It was previously shown, that catalyst 1a converts terminal secondary propargyl alcohols with various nucleophiles in a redox-isomerization/Michael addition cascade process (Scheme 1). As expected, the conversion of secondary substrates 2e–g with nucleophiles A–D in presence of catalyst 1a and TFA as an acidic promoter proceeds via redox-isomerization product 8 and leads to the formation of Michael addition products 3 or 4 in most cases. In contrast, catalyst of type 7 do not catalyze conversions of secondary alcohols 2e–g, neither in the presence nor in the absence of an acidic promoter (Scheme 6; Table 4). This is in accordance with further preliminary examinations regarding the catalytic activity of complexes 7 towards various terminal secondary propargyl alcohols.

The activation of terminal substrates 2 by complexes of type 1 occurs by the initial formation of alkynyl species I (Scheme 5) as it was shown by labeling experiments. We assume, that the following 1,2-H-shift is initiated by intra-

| Table 1. Formation of compound 5Aa applying different catalysts. |
|---|
| No | catalyst | promoter | conditions | Yield 5Aa |
|---|---|---|---|---|
| 1 | none | TFA | 100 °C, 5 h | n.c. |
| 2 | 1a | none | 100 °C, 5 h | 31%[a] |
| 3 | 1a | none | 100 °C, 5 h | 82%[b] |
| 4 | Ru₄(CO)₁₉ | TFA | 170 °C, 15 min | 19%[c] |
| 5 | Ru₄(CO)₁₉ | TFA | 170 °C, 15 min | 5%[d] |
| 6 | [Ru(CO)₃Cl]₂ | TFA | 100 °C, 5 h | 3%[e] |
| 7 | [Ru(CO)₃Cl]₂ | TFA | 170 °C, 15 min | 4%[f] |
| 9 | Tcc | TFA | 100 °C, 5 h | 10%[g] |
| 10 | Tcc | TFA | 170 °C, 15 min | 12%[h] |
| 11 | 7j | TFA | 100 °C, 5 h | 15%[i] |
| 12 | 7j | none | 100 °C, 5 h | 19%[j] |
| 13 | 7j | none | 170 °C, 15 min | 8%[k] |

n.c. = no conversion. [a] Substrate concentration 1.0 M. [b] Yield determined by NMR using an internal standard. [c] Isolated yield.

| Table 2. Formation of compound 5Ba applying different catalysts. |
|---|
| No | catalyst | promoter | concentration | conversion | Yield 5Ba |
|---|---|---|---|---|---|
| 1 | 1a | TFA | 1.0 M | 100% | 91%[l] |
| 2 | 1a | TFA | 1.0 M | 98% | 87%[m] |
| 3 | 1a | TFA | 0.5 M | 79% | 69%[n] |
| 4 | 1a | TFA | 0.25 M | 56% | 45%[o] |
| 5 | 1a | none | 0.25 M | 58% | 36%[p] |
| 6 | 7j | none | 0.25 M | 30% | 25%[q] |
| 7 | 7j | none | 0.25 M | 32% | 24%[r] |
| 8 | 7j | none | 0.25 M | 50% | 42%[s] |
| 9 | 7j | none | 0.25 M | 53% | 41%[t] |
| 10 | 7j | none | 0.25 M | 83% | 73%[u] |
| 11 | 7j | none | 1.0 M | 95% | 70%[v] |
| 12 | 7j | none | 0.25 M | 24% | 17%[w] |
| 13 | 7j | none | 0.25 M | 32% | 24%[x] |
| 14 | 7j | none | 0.25 M | 59% | 54%[y] |
| 15 | 7j | none | 0.25 M | 34% | 19%[z] |
| 16 | 7j | none | 0.25 M | 42% | 35%[{a}] |
| 17 | 7j | TFA | 0.25 M | 27% | 22%[|] |
| 18 | 7j | none | 1.0 M | 100% | 89%[}]
| 19 | 7j | none | 0.25 M | 37% | 23%[~] |
| 20 | 7j | none | 0.25 M | 27% | 15%[] |
| 21 | 7j | none | 0.25 M | 35% | 21%[] |
| 22 | 7j | none | 0.25 M | 23% | 18%[] |

[a] determined by NMR via remained B using an internal standard. [b] 100 °C, 5 h. [c] 170 °C, 15 min. [d] Isolated yield. [e] Yield determined by NMR using an internal standard.
molecular protonation of the alkyne unit via the ligands acidic hydroxyl group. Complexes of type 7 also activate terminal substrates 2 as alkynyl species (I-7), but no redox-isomerization takes place, presumably due to the lower acidity of the ligands amino function (Scheme 7).

We previously reported, that complex 1a catalyze the cycloaddition of 1,3-dicarbonyl compounds with some internal secondary propargyl alcohols. This conversion is especially interesting with substrates containing an additional alkenyl substituent like 2h, since the diene product (6Bh) can be further transformed by a [2+4]-cycloaddition in a one pot.

### Table 3. Products from alcohols 2a–d with nucleophiles A–D catalyzed by different catalysts (substrate concentration 1.0 M).

| catalyst | nucleophile | products from 2a | products from 2b | products from 2c | products from 2d |
|----------|-------------|-----------------|-----------------|-----------------|-----------------|
| 1a A     | 5AA         | 5Ab             | 5Ac             | 5Ad             |
|          |             | (82%)           | (49%)           | (89%)           | (97%)           |
| 1a B     | 5Ba         | 5Bb             | 5Bc             | 5Bd             |
|          |             | (91%)           | (90%, dr 5:4)   | (54%, dr 5:2)   | (93%, dr 5:1)   |
| 1a C     | 5Ca         | 5Cb             | 5Cc             | 5Cd             |
|          |             | (86%)           | (61%, dr 15:1)  | (92%, dr 15:1)  | (98%, dr 17:1)  |
| 1a D     | 5Da         | 5Db             | 5Dc             | 5Dd             |
|          |             | (82%)           | (80%, dr 2:1)   | (80%, dr 2:1)   | (98%, dr 3:1)   |
| 7j A     | 5Aa         | 5Ab             | 5Ac             | 5Ad             |
|          |             | (19%)           | (8%, dr 15:1)   | (15%)           |
| 7j B     | 5Ba         | 5Bb             | 5Bc             | 5Bd             |
|          |             | (89%)           | (67%, dr 2:1)   | (55%, dr 1:1)   | (85%, dr 3:2)   |
| 7j C     | 5Ca         | 5Cb             | 5Cc             | 5Cd             |
|          |             | (80%)           | (62%, dr 6:1)   | (81%, dr 4:1)   | (92%, dr 2:1)   |
| 7j D     | 5Da         | 5Db             | 5Dc             | 5Dd             |
|          |             | (39%)           | (80%, dr 2:1)   | (90%, dr 5:2)   |

[a] Compound previously reported in Ref. [4]e. [b] Compound previously reported in Ref. [4]c. [c] Compound previously reported in Ref. [4]b. [d] Prepared by conventional heating (100°C, 5 h). [e] 180°C, 5 min. [f] 170°C, 15 min.

### Scheme 5. Conversion of terminal tertiary substrates with nucleophiles A–D.

![Conversion of terminal tertiary substrates with nucleophiles A–D.](image)

### Table 4. Products of alcohols 2e–g with nucleophiles A–D catalyzed by catalyst 1a (substrate concentration 1.0 M; 170°C, 15 min).

| catalyst | nucleophile | products from 2e | products from 2f | products from 2g |
|----------|-------------|-----------------|-----------------|-----------------|
| 1a A     | 4Ae         | 3Af             | 3Ag             |
|          |             | (85%)           | (68%)           | (trace)         |
| 1a B     | 3Be         | 8Ff             | 8Gg             |
|          |             | (64%)           | (26%)           | (96%)           |
| 1a C     | 3Ce         | 8Ff             | 8Gg             |
|          |             | (48%)           | (95%)           | (97%)           |
| 1a D     | 4De         | 8Ff             | 8Gg             |
|          |             | (45%, dr 2:1)   | (28%)           |
| 7a–n     | A–D         | n.c.            | n.c.            | n.c.            |

n.c. = no conversion. [a] Compound previously reported in Ref. [4]e. [b] Compound previously reported in Ref. [4]a.
process (Scheme 8). Byproduct 9 Bh is formed with low trans-selectivity by alkylation of the nucleophile and subsequent 5-exo-trig cyclization. Comparable yields and selectivities are obtained at 100 °C (5 h) or at 170 °C (μW, 15 min) if catalyst 1a (2 mol %) and TFA (4 mol %) are applied. The reaction rate decreases with higher dilution (Table 5, entries 1–3). Complexes of type 7 also catalyze this transformation, but with lower activity and chemoselectivity. The complexes of type 7 show hardly any differences in activity among one another (Table 5, entries 4–10).

Now, we wanted to apply this transformation to terpenoid-derived propargyl alcohols 2i–2l. With regard to the synthesis of phloroglucinol-terpenoid adducts, plorogluclorin derivative E was used as an additional CH-acidic nucleophile (Scheme 9).

Unfortunately, we found the substrate scope of the original procedure to be very limited. Conversions of terpene derivatives 2i–l with nucleophiles A–E applying catalyst 1a (2 mol %) and TFA (4 mol %) lead to extensive decomposition and only small amounts of dihydropyranes 6 are isolated. In contrast, propargyl alcohols 2i, 2k and 2l are converted in moderate to good yields with nucleophiles B, C or E if catalyst 7j without an acidic promoter is applied. Only small quantities of products 6 are obtained from alcohol 2j. Conversions of internal secondary propargyl alcohols 2i–l with 1,3-dione A are not catalyzed by complex 7j, whereas nucleophile D leads to extensive decomposition. Occasionally, small amounts of the oxidized by-products 10 are isolated. Uncyclized products 11 are formed from nucleophile E in some cases (Table 6; Figure 3).

**Conclusions**

In principle, triaminocyclopentadienyl ruthenium complexes (7) are useful catalysts for cascade conversions of propargyl alcohols. Their synthesis is straightforward and enantiopure derivatives for future applications in asymmetric catalysis are easily accessible. However, the simpler diaminocyclopentadiene-none catalyst 1a is superior to complexes of type 7 in terms of converting terminal tertiary substrates. Moreover, redox-isomerization processes of terminal secondary derivatives are not catalyzed at all by the new complexes (7). In contrast, introducing the third amine-function on the cyclopentadienyl ligand has a significant effect on the conversion of internal substrates. The new catalysts (7) extend the scope of cascade conversions of internal 1-alkenylpropargyl alcohols, originally catalyzed by ruthenium catalyst 1a, to various terpenoid-derived derivatives. In addition, reactions catalyzed by complexes of type 7 are applicable for the conversion of acid-sensitive substrates, since they do not require an acidic

**Table 5. Formation of compounds 6 Bh and 9 Bh applying different catalysts**

| No | catalyst | promoter | conc. | 6 Bh | 9 Bh |
|----|----------|----------|------|------|------|
| 1a | 1a       | TFA      | 1.0 M| 62 %| 29 %| dr 3:2|
| 2h | 2h       | TFA      | 1.0 M| 66 %| 24 %| dr 3:2|
| 3h | 3a       | TFA      | 0.5 M| 43 %| 18 %| dr 3:2|
| 4h | 4c       | none     | 0.5 M| 19 %| 23 %| dr 4:3|
| 5h | 5d       | none     | 0.5 M| 20 %| 23 %| dr 2:1|
| 6h | 6e       | none     | 0.5 M| 18 %| 20 %| dr 2:1|
| 7h | 7f       | none     | 0.5 M| 17 %| 23 %| dr 4:3|
| 8h | 8g       | none     | 0.5 M| 22 %| 15 %| dr 2:1|
| 9h | 9h       | none     | 0.5 M| 19 %| 24 %| dr 2:1|
| 10h| 10j      | none     | 1.0 M| 40 %| 35 %| dr 2:1|

[a] 100 °C, 5 h. [b] 170 °C, 15 min. [c] Isolated yield. [d] Yield determined by NMR using an internal standard.
promoter. A broad range of terpenoid and phloroglucinol adducts are accessible by complementary application of both types of catalysts. The compounds obtained are suitable as structural building blocks for the synthesis of related bioactive natural products and analogues. Further applications of the new catalysts, especially in the context of asymmetric catalysis is the subject of our ongoing research.

Experimental Section

See the Supporting Information for full experimental procedures and characterization data of all products.

General Information

All reactions were carried out in a dry atmosphere under argon. The chemicals used were dried and purified according to common
procedures. Products were identified by spectroscopic analysis (1H NMR, 13C NMR, IR, MS, HRMS). Multiplicity was determined by DEPT spectra for all compounds. Infrared spectra were obtained with a PERKIN-ELMER FTIR 2000 or a VERTEX 70 V. NMR spectra were recorded on a BRUKER DXP 400 or a BRUKER AVANCE 600 spectrometer. MS data was obtained with a FINNIGAN SSQ 7000 (EI) or a WATERS ACQUITY UPLC-MS-H/CLASS (ESI) and HRMS data was obtained on a FINNIGAN MAT 95. Specific optical rotation of chiral compounds was measured on an ANTON PAAR MCP 150 polarimeter. Reactions using microwave irradiation were performed in an ANTON PAAR MONOWAVE 300 reactor.

General procedure for the preparation of catalysts 7: Ru(CO)₂(C₅H₅N)BF₄: 1H NMR (600 MHz, CDCl₃): \(\delta = 8.13 \text{ (br, d, } J = 7.2 \text{ Hz, } 2 \text{H})\), 7.50–7.45 (m, 4H), 7.42 (br, t, \(J = 7.0 \text{ Hz, } 1 \text{H})\), 7.10–7.09 (m, 3H), 6.75–6.73 (m, 2H), 3.66 (t, \(\nu = 6.5, 3.7 \text{ Hz, } 1 \text{H})\), 3.21 (s, 1H), 2.67 (dd, \(J = 6.5, 3.6 \text{ Hz, } 1 \text{H})\), 2.16 ppm (s, 6H); MS (ESI): m/z (%): 579 (16), 566 [M–BF₄]⁻ (20), 531 (46), 529 (100), 528 [M–CO–BF₄]⁻ (62), 527 (55), 526 (40), 501 (65), 500 (45), 499 (34), 497 (51), 496 (40), 471 (80), 463 (90), 468 (75), 467 (58), 466 (40); HRMS (EI): m/z calcd for C₇H₫N₅O₂RuBF₄: 728.1220 [M–CO–BF₄]⁻; found: 728.1224.

7c (C₁₀H₈N₅O₄RuBF₄): 1H NMR (600 MHz, CDCl₃): \(\delta = 7.90–7.29 \text{ (m, } 10H)\), 7.10–7.09 (m, 6H), 6.75–6.73 (2H), 3.66 (s, 3H), 3.54 (dd, \(J = 6.7, 3.7 \text{ Hz, } 1 \text{H})\), 3.51 (dd, \(J = 6.6, 3.8 \text{ Hz, } 1 \text{H})\), 3.48 (d, \(J = 5.7 \text{ Hz, } 2 \text{H})\), 2.68 (dd, \(J = 6.6, 3.9 \text{ Hz, } 1 \text{H})\), 2.65 (dd, \(J = 6.6, 3.8 \text{ Hz, } 1 \text{H})\), 2.10 ppm (s, 6H); 13C NMR (150 MHz, CDCl₃): \(\delta = 192.8 \text{ (3C), 140.2 (C), 135.3 (C), 135.2–133.8 (br, 2CH), 130.3 (2CH), 128.6 (2CH), 127.8 (2CH), 127.6 (br, 2C), 126.9 (2CH), 118.4 (2C), 65.5 (2C), 49.8 (2C), 49.1 (CH₁), 41.4 ppm (2CH); IR (ATR) \nu = 3339 (w), 3059 (w), 2990 (w), 2924 (w), 2861 (w), 1728 (m), 1586 (m), 1452 (m), 1275 (s), 1121 (m), 1055 (s), 741 (m), 697 cm⁻¹ (m); MS (ESI): m/z (%): 592 [M–BF₄]⁻ (16), 591 (10), 566 (30), 565 (18), 544 [M–CO–BF₄]⁻ (57), 563 (33), 562 (25), 561 (21), 408 (23), 407 (32), 406 (100); HRMS (EI): m/z calcd for C₁₀H₈N₅O₄Ru: 564.1221 [M–CO–BF₄]⁻; found: 564.1236.

7d (C₁₁H₉N₅O₄RuBF₄): 1H NMR (600 MHz, CDCl₃): \(\delta = 7.88–7.29 \text{ (m, } 10H)\), 7.12–7.05 (m, 3H), 6.60 (d, \(J = 7.0 \text{ Hz, } 2 \text{H})\), 3.53 (dd, \(J = 6.6, 3.6 \text{ Hz, } 1 \text{H})\), 3.50 (dd, \(J = 6.5, 3.7 \text{ Hz, } 1 \text{H})\), 3.21 (s, 1H), 2.67 (dd, \(J = 6.6, 3.8 \text{ Hz, } 1 \text{H})\), 2.64 (dd, \(J = 6.5, 3.6 \text{ Hz, } 1 \text{H})\), 2.48 (t, \(J = 6.7 \text{ Hz, } 2 \text{H})\), 2.32 (t, \(J = 6.7 \text{ Hz, } 2 \text{H})\), 2.11 ppm (s, 6H); 13C NMR (150 MHz, CDCl₃): \(\delta = 192.6 \text{ (3C), 140.8 (C), 136.1 (C), 135.4–133.6 (br, 2CH), 132.2–131.1 (br, 2CH), 130.0 (2CH), 129.7 (4CH), 128.6 (2CH), 128.1 (2CH), 127.6 (br, 2C), 126.6 (2CH), 118.0 (2C), 68.0 (2C), 49.7 (2C), 45.6 (CH₂), 41.3 (CH₂), 34.3 ppm (CH); IR (ATR) \nu = 3362 (w), 3059 (w), 2992 (w), 2859 (w), 1990 (m), 1044 (m), 695 cm⁻¹ (m); MS (ESI): m/z (%): 579 (28), 578 [M–CO–BF₄]⁻ (16), 523 (21), 522 (37), 511 (32), 520 (33), 519 (24), 480 (22), 479 (36), 478 (21), 466 (29), 332 (35), 316 (100); MS (EI): m/z (%): 598 (25), 580 (33), 579 (60), 578 [M–CO–BF₄]⁻ (35), 577 (36), 576 (28), 575 (22), 538 (33), 537 (45), 536 (44), 535 (24), 534 (33), 282 (29), 171 (33); HRMS (EI): m/z calcd for C₁₁H₈N₅O₄RuBF₄: 578.1377 [M–CO–BF₄]⁻; found: 578.1384.
7) ([C\textsubscript{6}H\textsubscript{5}NO\textsubscript{2}]\textsubscript{2}RuBF\textsubscript{3}]: H NMR (600 MHz, CDCl\textsubscript{3}); \(\delta = 8.00–7.35\) (m, 10H), 3.82 (t, \(J = 5.4\) Hz, 3H), 3.60–3.56 (m, 2H, H\textsubscript{2}H), 3.51 (d, \(J = 13.8, 6.9, 3.4\) Hz, 1H), 3.44 (d, \(J = 8.3, 7.0\) Hz), 3.37 (dt, \(J = 8.2, 6.5\) Hz, 1H), 2.73–2.68 (m, 2H), 2.34 (dd, \(J = 12.9, 5.6, 3.5\) Hz, 1H), 2.17 (s, 3H), 2.16 (s, 3H), 2.13 (d, \(J = 12.7, 7.0\)), 5.3 Hz, 1H), 1.66–1.51 (m, 3H), 1.09–1.03 ppm (m, 1H).

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Conflict of Interest

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