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Nickel(0)-mediated [2+2+1] cyclization reaction of chromium carbene complexes and internal alkynes

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Dedicated to Professor Günther Wilke for his contribution to the field of organonickel chemistry

Abstract—Alkyl, aryl, and heteroaryl chromium Fischer carbene complexes undergo Ni(0)-mediated [2+2+1] cyclization reaction with internal unactivated and electron-poor internal alkynes to yield highly substituted cyclopentadienes with complete regioselectivity in most cases. The intramolecular version of this cyclization has been accomplished with 1,8-diphenyl-1,7-octadiyne to produce indene derivatives. This three-component [2+2+1] cyclization represents a very uncommon process in the chemistry of Fischer carbene complexes.
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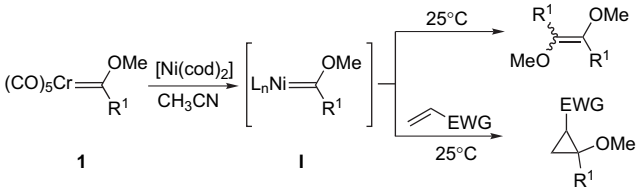
1. Introduction

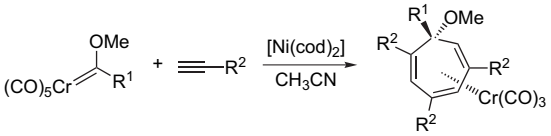
In the last years Fischer carbene complexes have become useful reagents in synthetic organic chemistry.[1] Although these type of carbene complexes are well known for a number of transition metals, only a few nickel(0) carbene complexes have been hitherto reported. Wilke et al.[2] and Pinhas and Simunic[3] described the preparation and characterization of the complexes $[L_2Ni{=}C(NR_2)Ph]$ and $[(CO)_3Ni{=}C(OSiMe_3)Bu]$, respectively.[4] We and others have studied recently the transmetalation reaction[5] as a convenient route to access new carbene complexes of late transition metals, such as Cu(I),[6] Pd(0),[7] and Rh(I) .[8] This methodology proved to be also useful for the generation of nickel(0) alkoxycarbene complexes **I** from the corresponding chromium complexes **1** and $[Ni(cod)_2]$. The existence of the species **I** is validated by (i) the room temperature thermal dimerization of the carbene ligand, and (ii) its capability to cyclopropanate electron-poor alkenes at room temperature (Scheme 1).[9,10]



1 I

Scheme 1.

More importantly, the different nature of chromium and nickel allowed us to discover novel reaction patterns in the transition metal carbene chemistry area.[9,11] Specifically, we found that complexes **1** undergo a very unusual [2+2+2+1] cyclization reaction with terminal alkynes to give selectively chromium cycloheptatriene complexes (Scheme 2).[9]



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Scheme 2.

This result sharply contrasts with those found previously after extensive studies with the group 6 carbene precursors themselves. In this respect, Figure 1 summarizes the most common cyclization modes of group 6 Fischer carbene complexes toward terminal and internal alkynes. Thus, metal aryl carbenes afford variable mixtures of naphthol, indene, cyclobutenone, and furan derivatives,[12] while chromium alkyl carbenes have been reported to yield substituted cyclopentenones.[13]

We report herein that the reaction of chromium carbene complexes with internal alkynes (Fig. 2) in the presence of $[Ni(cod)_2]$ neither proceeds as outlined in Figure 1 nor via a [2+2+2+1] cyclization as for terminal alkynes (Scheme 2), but a new reaction pathway for Fischer carbene complexes, namely the [2+2+1] cyclization, actually operates.[14] It will be also noted that the mode of assembling of both alkyne units into the resulting cyclopentadiene depends primarily on the electronic demand of the alkyne.

Keywords: Carbene complexes; Chromium(0); Nickel(0); Carbene transfer; Alkynes; Cyclopentadienes; Three-component process.
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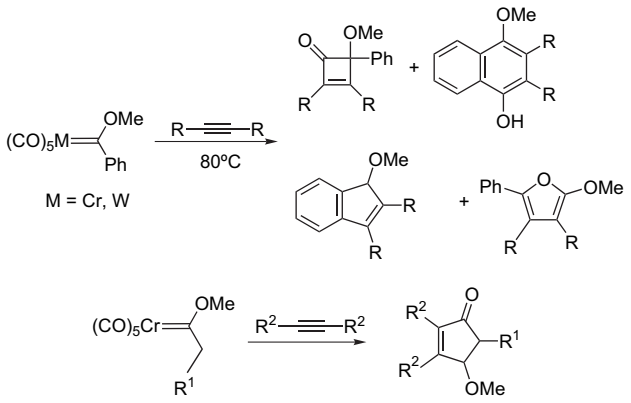


Figure 1.

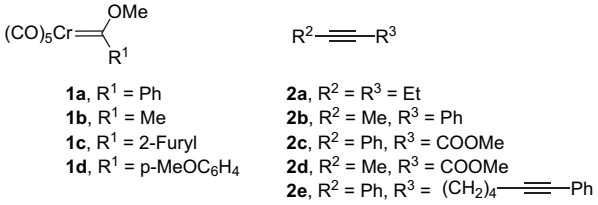
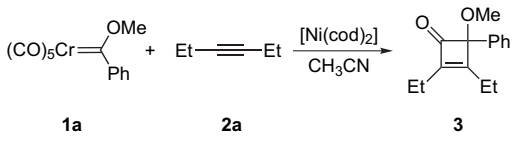


Figure 2.

2. Results and discussion

First we examined the reaction of chromium phenyl carbene complex **1a** with 3-hexyne **2a** and [Ni(cod)$_2$] (molar ratio 1:3:1) in acetonitrile. The reagents were mixed at −10 °C and allowed to reach room temperature during 2 h. The reaction mixture was chromatographed giving rise to the [2+1+1] cycloadduct **3** (25% yield)[12] as the sole isolable reaction product (Scheme 3).[15]

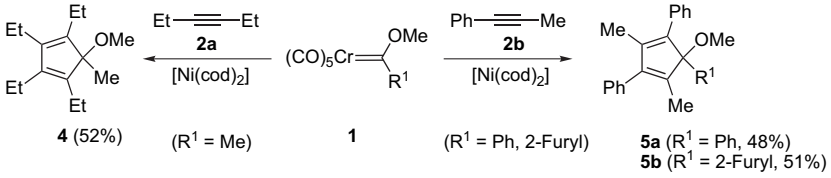


Scheme 3.

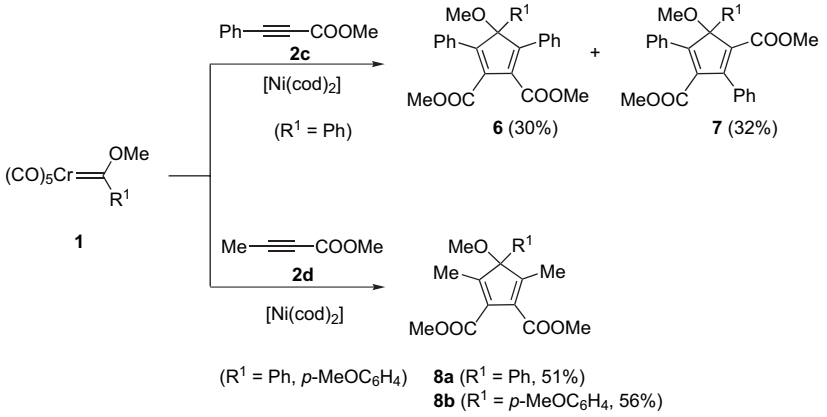
Interestingly, starting from appropriate carbene complex/alkyne combinations resulted in the complete inhibition of cyclobutenone formation in favor of a three-component [2+2+1] cyclization reaction (Scheme 4). Thus, [Ni(cod)$_2$] was added to a solution of 3-hexyne and methylcarbene **1b** (R^1=Me) in acetonitrile at −10 °C (molar ratio 1:2.5:1) and the mixture allowed to reach room temperature. Removal of solvent and alkyne excess followed by column chromatography purification afforded the densely substituted cyclopentadiene **4** in 52% yield.

The regioselectivity of this rare cyclization was then tested with 1-phenyl-1-propyne **2b**. In this case, the reaction of such an alkyne with carbene complexes **1a** (R^1=Ph) and **1c** (R^1=2-furyl) under the above reaction conditions led to unsymmetrical cycloadducts **5a**,**b** (48 and 51% yield) as a sole isomer in each case.

It was delightful to find that alkynes with an electron-withdrawing substituent are productive components in this reaction to provide functionalized cycloadducts (Scheme 5). For instance, the cyclization of the carbene complex **1a** and methyl phenylpropynoate **2c** resulted in the formation of a mixture of symmetrical and unsymmetrical cyclopentadienes **6** and **7**, respectively, in 62% yield (**6**/**7** ratio = 1:1). In contrast, the cyclization between **1a**,**d** and methyl 2-butynoate **2d** resulted in the regioselective formation of the cycloadducts **8a**,**b** in 51–56% yield. The structural assignment of 1,4-diphenyl-1,3-cyclopentadiene **6** and 1,4-dimethyl-1,3-cyclopentadiene **8** over 2,3-diphenyl- and



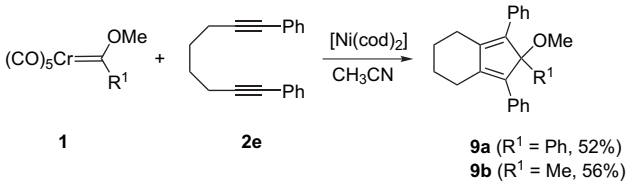
Scheme 4.



Scheme 5.

2,3-dimethylcyclopentadiene regioisomers (not shown) becomes apparent from NMR experiments (including HMQC, HMBC, and NOESY).

The scope of this cyclization could be successfully extended to the intramolecular version, thus allowing to access bicyclic cyclopentadienes (Scheme 6). This task was brought about by reacting carbene complexes **1a**,**b** and 1,8-diphenyl-1,7-octadiyne **2e** under the above reaction conditions to produce tetrahydroindenes **9a**,**b** (52–56% yield).



Scheme 6.

Concerning the reaction pathway, it should be noted that a common mechanism cannot operate in all cases since a divergent regiochemistry is observed depending on the nature of the alkyne (compare cyclopentadienes **5** *vs* **8**). A tentative rationale for the alkynes 1-phenyl-1-propyne **2b** and methyl 2-butynoate **2d** is outlined in Scheme 7. The chromium–nickel exchange to form the nickel carbene species **I** is assumed to be the common initial step. Two consecutive regioselective insertion reactions of 1-phenyl-1-propyne into the nickel–carbon double bond would generate the 1-nickela-1,3,6-hexatriene **II**, which would produce the final cycloadducts **5** upon cyclization to the nickelacycle **III** and Ni(0) reductive elimination (via *A*).[16] On the contrary, the symmetrical structure of cycloadducts **8** makes this mechanism unsatisfactory. On the ground of a recent proposal by Ni and Montgomery involving nonheteroatom stabilized carbene nickel(0) species and dienynes,[17] we propose that the formation of the symmetrical products **8** begins with the oxidative co-cyclization of nickel carbene complex **I** with two alkyne units to form regioselectively the nickelacyclopentadiene **IV** (via *B*).[18] Then, carbene insertion into the nickel–carbon bond would allow production of nickelacyclohexadiene **V**, which would provide **8** by reductive elimination.[19] When phenylpropiolate, instead of methylpropiolate is employed, we suspect that both mechanisms, double insertion (via *A*) and cyclometalation (via *B*), are productive yielding **7** and **6**, respectively.[20,21] We have no further evidences so as to decide the actual mechanism in the case of the intramolecular cyclization. While the single, neutral alkyne would suggest the insertion route, the entropic argument would facilitate the assembling of both reaction components and thus would favor the nickelacyclopentadiene pathway.

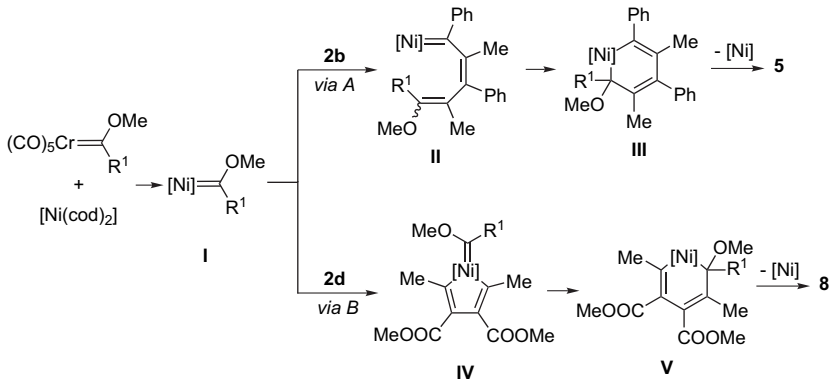
3. Conclusion

In conclusion, we have developed a highly efficient inter- and intramolecular [2+2+1] cyclization of chromium (methoxy)carbene complexes with internal alkynes and diynes in the presence of [Ni(cod)$_2$]. Except for methyl phenylpropiolate, the reaction is completely regioselective in all cases tested. Depending on the electronic nature of the alkyne different reaction pathways are proposed beginning with a nickel(0) Fischer carbene complex, namely carbene/alkyne insertion and alkyne/nickel cyclometalation. This approach provides a convenient entry to highly substituted cyclopentadiene and indene derivatives.[22] Further studies aimed at investigating the scope of this new reaction are currently ongoing in our laboratories.

4. Experimental

4.1. General methods

All reactions were carried out under N_2 using standard Schlenck techniques. Fischer carbene complexes **1a–d**[23] and 1,8-diphenyl-1,7-octadiyne[24] were prepared according to literature procedures. All common reagents were obtained from commercial suppliers and used without further purification unless otherwise indicated. Acetonitrile was distilled from CaH_2. TLC was performed on aluminum-backed plates coated with silica gel 60 with F254 indicator. Flash column chromatography was carried out on silica gel 60 (230–240 mesh). ^{1}H NMR (300 MHz) and ^{13}C NMR (70.5 MHz) spectra were measured in $CDCl_3$ at room temperature on a Bruker AC-300 instrument, with tetramethylsilane (δ=0.0, ^{1}H NMR) and $CDCl_3$ (δ=77.0, ^{13}C NMR) as internal standard. Elemental analyses were carried out on Perkin–Elmer 2400 and Carlo Erba 1108 microanalyzers.



Scheme 7.

4.2. General procedure for the nickel(0)-mediated [2+2+1] reaction of Fischer carbene complexes 1 with internal alkynes

To a solution of complex **1** (1.0 equiv) and alkyne (2.5 equiv) or diyne (1.1 equiv) in acetonitrile was added [Ni(cod)$_2$] (1.1 equiv) at −10 °C. The reaction mixture was allowed to reach room temperature during 2 h. The solvent was then removed and the resulting residue was subjected to flash chromatography (SiO_2, mixtures of hexane/ethyl acetate) to give pure cyclopentadiene and indene derivatives.

4.2.1. 1,2,3,4-Tetraethyl-5-methoxy-5-methyl-1,3-cyclopentadiene (4). The general procedure was followed using complex **1b** (125 mg, 0.5 mmol), 3-hexyne (103 mg, 1.25 mmol), and [Ni(cod)$_2$] (151 mg, 0.55 mmol) in acetonitrile (7 ml). Final chromatographic purification using a 10:1 mixture of hexane/ethyl acetate as eluent afforded the *title compound* **4** (58 mg, 52%) as a colorless oil; [Found: C, 81.22; H, 11.70. $C_{15}H_{26}O$ requires C, 81.02; H, 11.79%]; δ_H (300 MHz, $CDCl_3$) 2.84 (3H, s, OMe), 2.29–2.10 (8H, m, CH_2–CH_3), 1.24 (3H, s, Me), 1.10 (6H, t, *J* 7.9 Hz, CH_2–CH_3), 1.06 (6H, t, *J* 7.9 Hz, CH_2–CH_3); δ_C (70.5 MHz, $CDCl_3$) 141.6, 141.4, 89.4, 51.1, 20.4, 18.6, 17.6, 14.8, 13.8.

4.2.2. 5-Methoxy-1,3-dimethyl-2,4,5-triphenyl-1,3-cyclopentadiene (5a). The general procedure was followed using complex **1a** (156 mg, 0.5 mmol), 1-phenyl-1-propyne (145 mg, 1.25 mmol), and [Ni(cod)$_2$] (151 mg, 0.55 mmol) in acetonitrile (7 ml). Final chromatographic purification using a 20:1 mixture of hexane/ethyl acetate as eluent afforded the *title compound* **5a** (84 mg, 48%) as a colorless oil; [Found: C, 88.52; H, 6.94. $C_{26}H_{24}O$ requires C, 88.60; H, 6.86%]; δ_H (300 MHz, $CDCl_3$) 7.37–7.02 (15H, m, Ph), 3.27 (3H, s, OMe), 2.11 (3H, s, Me), 1.58 (3H, s, Me); δ_C (70.5 MHz, $CDCl_3$) 144.2, 142.7, 141.4, 140.3, 140.1, 135.5, 135.3, 129.3, 128.2, 128.1, 128.0, 127.9, 127.0, 126.6, 126.2, 125.3, 94.4, 50.9, 14.3, 10.2.

4.2.3. 5-(2-Furyl)-5-methoxy-1,3-dimethyl-2,4-diphenyl-1,3-cyclopentadiene (5b). The general procedure was followed using complex **1c** (151 mg, 0.5 mmol), 1-phenyl-1-propyne (145 mg, 1.25 mmol), and [Ni(cod)$_2$] (151 mg, 0.55 mmol) in acetonitrile (7 ml). Final chromatographic purification using a 40:1 mixture of hexane/ethyl acetate as eluent afforded the *title compound* **5b** (87 mg, 51%) as a colorless oil; [Found: C, 84.25; H, 6.37. $C_{24}H_{22}O_2$ requires C, 84.18; H, 6.48%]; δ_H (300 MHz, $CDCl_3$) 7.31 (1H, d, *J* 1.7 Hz, Fu), 7.30–7.15 (10H, m, Ph), 6.46 (1H, dd, *J* 3.2 and 1.7 Hz, Fu), 6.34 (1H, dd, *J* 3.2 and 0.6 Hz, Fu), 3.56 (3H, s, OMe), 1.87 (3H, s, Me), 1.79 (3H, s, Me); δ_C (70.5 MHz, $CDCl_3$) 162.5, 153.6, 141.9, 141.4, 139.5, 135.9, 135.8, 129.3, 128.4, 127.9, 127.4, 126.7, 118.8, 110.1, 107.5, 63.7, 60.84, 12.0, 10.8. HRMS (EI) calcd for $C_{24}H_{22}O_2$: 342.1620; found 342.1635 $[M]^+$.

4.2.4. Reaction of complex 1a and methyl phenylpropynoate 2c. The general procedure was followed using complex **1a** (156 mg, 0.5 mmol), methyl phenylpropynoate (200 mg, 1.25 mmol), and [Ni(cod)$_2$] (151 mg, 0.55 mmol) in acetonitrile (7 ml). Final chromatographic purification using a 5:1 mixture of hexane/ethyl acetate as eluent afforded compounds **6** and **7**.

4.2.4.1. 5-Methoxy-2,3-bis(methoxycarbonyl)-1,4,5-triphenyl-1,3-cyclopentadiene (6). The *title compound* **6** was isolated as a yellowish oil (66 mg, 30%); [Found: C, 76.48; H, 5.37. $C_{28}H_{24}O_5$ requires C, 76.35; H, 5.49%]; δ_H (300 MHz, $CDCl_3$) 7.45–7.13 (15H, m, Ph), 3.78 (6H, s, COOMe), 3.34 (3H, s, OMe); δ_C (70.5 MHz, $CDCl_3$) 167.7, 152.3, 138.0, 136.9, 134.5, 128.7, 128.1, 127.9, 127.7, 96.3, 52.3, 51.7.

4.2.4.2. 5-Methoxy-1,3-bis(methoxycarbonyl)-2,4,5-triphenyl-1,3-cyclopentadiene (7). The *title compound* **7** was isolated as a yellowish oil (70 mg, 32%); [Found: C, 76.24; H, 5.52. $C_{28}H_{24}O_5$ requires C, 76.35; H, 5.49%]; δ_H (300 MHz, $CDCl_3$) 7.57–7.22 (15H, m, Ph), 3.56 (3H, s, OMe), 3.44 (3H, s, OMe), 3.42 (3H, s, OMe); δ_C (70.5 MHz, $CDCl_3$) 166.2, 162.7, 154.3, 153.3, 136.6, 135.8, 135.5, 133.6, 131.8, 129.2, 128.6, 128.3, 128.2, 127.8, 127.7, 127.4, 125.1, 94.3, 52.1, 52.0, 51.0.

4.2.5. 5-Methoxy-2,3-bis(methoxycarbonyl)-1,4-dimethyl-5-phenyl-1,3-cyclopentadiene (8a). The general procedure was followed using complex **1a** (156 mg, 0.5 mmol), methyl butynoate (123 mg, 1.25 mmol), and [Ni(cod)$_2$] (151 mg, 0.55 mmol) in acetonitrile (7 ml). Final chromatographic purification using a 5:1 mixture of hexane/ethyl acetate as eluent afforded the *title compound* **8a** (81 mg, 51%) as a yellowish oil; [Found: C, 68.53; H, 6.51. $C_{18}H_{20}O_5$ requires C, 68.34; H, 6.37%]; δ_H (300 MHz, $CDCl_3$) 7.33–7.03 (5H, m, Ph), 3.60 (6H, s, COOCH_3), 3.23 (3H, s, OCH_3), 2.40 (6H, s, C≡C–CH_3); δ_C (70.5 MHz, $CDCl_3$) 163.5, 154.8, 138.2, 137.5, 127.7, 126.7, 124.9, 92.1, 51.6, 51.1, 13.2.

4.2.6. 5-Methoxy-2,3-bis(methoxycarbonyl)-5-(4-methoxyphenyl)-1,4-dimethyl-1,3-cyclopentadiene (8b). The general procedure was followed using complex **1d** (171 mg, 0.5 mmol), methyl butynoate (123 mg, 1.25 mmol), and [Ni(cod)$_2$] (151 mg, 0.55 mmol) in acetonitrile (7 ml). Final chromatographic purification using a 5:1 mixture of hexane/ethyl acetate as eluent afforded the *title compound* **8b** (97 mg, 56%) as a yellowish oil; [Found: C, 65.73; H, 6.29. $C_{19}H_{22}O_6$ requires C, 65.88; H, 6.40%]; δ_H (300 MHz, $CDCl_3$) 7.26 (2H, d, *J* 8.9 Hz, Ar), 6.77 (2H, d, *J* 8.9 Hz, Ar), 3.77 (3H, s, $ArOCH_3$), 3.62 (6H, s, COOCH_3), 3.21 (3H, s, OCH_3), 2.38 (6H, s, C≡C–CH_3); δ_C (70.5 MHz, $CDCl_3$) 163.5, 158.3, 154.4, 138.0, 129.2, 126.0, 113.1, 91.8, 55.0, 51.6, 51.1, 13.2. HRMS (EI) calcd for $C_{19}H_{22}O_6$: 346.1416; found 346.1416 $[M]^+$.

4.2.7. 4,5,6,7-Tetrahydro-2-methoxy-1,2,3-triphenyl-2*H*-indene (9a). The general procedure was followed using complex **1a** (156 mg, 0.5 mmol), 1,8-diphenyl-1,7-octadiyne (142 mg, 0.55 mmol), and [Ni(cod)$_2$] (151 mg, 0.55 mmol) in acetonitrile (7 ml). Final purification using a 20:1 mixture of hexane/ethyl acetate afforded the *title compound* **9a** (98 mg, 52%) as a colorless oil; [Found: C, 88.92; H, 6.83. $C_{28}H_{26}O$ requires C, 88.85; H, 6.92%]; δ_H (300 MHz, $CDCl_3$) 7.29–7.12 (15H, m, Ph), 3.21 (3H, s, OMe), 2.88–2.72 (4H, m, C≡C–CH_2–CH_2), 1.84–1.73 (4H, m, C≡C–CH_2–CH_2); δ_C (70.5 MHz, $CDCl_3$) 141.2, 141.1, 140.6, 134.7, 127.9, 126.2, 125.2, 95.3, 51.0, 26.9, 23.6.

4.2.8. 4,5,6,7-Tetrahydro-2-methoxy-2-methyl-1,3-diphenyl-2*H*-indene (9b). The general procedure was

followed using complex **1b** (125 mg, 0.5 mmol), 1,8-diphenyl-1,7-octadiyne (142 mg, 0.55 mmol), and [Ni(cod)$_2$] (151 mg, 0.55 mmol) in acetonitrile (7 ml). Final purification using a 20:1 mixture of hexane/ethyl acetate afforded the *title compound* **9b** (88 mg, 56%) as a colorless oil; [Found: C, 87.42; H, 7.71. $C_{23}H_{24}O$ requires C, 87.30; H, 7.64%]; δ_H (300 MHz, $CDCl_3$) 7.49–7.30 (10H, m, Ph), 3.20 (3H, s, OMe), 2.91–2.75 (4H, m, C═C–CH_2–CH$_2$), 1.84–1.71 (4H, m, C═C–CH$_2$–CH_2), 1.38 (3H, s, Me); δ_C (70.5 MHz, $CDCl_3$) 140.0, 138.6, 135.4, 128.1, 127.8, 126.3, 91.5, 51.2, 26.1, 23.3, 23.1.

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14. (a) For an isolated example involving the [2+2+1] cyclization of pentacarbonyl[(*N*,*N*-dimethylamino)methylene]chromium with methyl acrylate and acrylonitrile, see: Sierra, M. A.; Soderberg, B.; Lander, P. A.; Hegedus, L. S. *Organometallics* **1993**, *12*, 3769; (b) For the thermal [2+2+1] cyclization of phenylallene and chromium carbene complexes, see: Aumann, R.; Uphoff, J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 357.
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19. The oxidative cyclometalation pathway (via *B*) is abandoned in the case of 1-phenyl-1-propyne as Eisch et al. observed that the nickel(0)-mediated cyclotrimerization product of 1-phenyl-1-propyne arises exclusively from the symmetrical nickelacyclopentadiene species. See, Eisch, J. J.; Damasevitz, G. A. *J. Organomet. Chem.* **1975**, *96*, C19.
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