Nickel-catalyzed skeletal transformation of tropone derivatives via C–C bond activation: catalyst-controlled access to diverse ring systems†

Takuya Kodama,†a,b Kanako Saitoa and Mamoru Tobisu‡a,b*

We report herein on nickel-catalyzed carbon–carbon bond cleavage reactions of 2,4,6-cycloheptatrien-1-one (tropone) derivatives. When a Ni/N-heterocyclic carbene catalyst is used, decarbonylation proceeds with the formation of a benzene ring, while the use of bidentate ligands in conjunction with an alcohol additive results in a two-carbon ring contraction with the generation of cyclopentadiene derivatives. The latter reaction involves a nickel–ketene complex as an intermediate, which was characterized by X-ray crystallography. The choice of an appropriate ligand allows for selective synthesis of four different products via the cleavage of a seven-membered carbocyclic skeleton. Reaction mechanisms and ligand-controlled selectivity for both types of ring contraction reactions were also investigated computationally.

Introduction

Transition metal-mediated selective cleavage of carbon–carbon (C–C) bonds has attracted the interest of researchers, since it would allow for the direct transformation of one of the most ubiquitous bonds in organic molecules.1 However, both the kinetic and thermodynamic stability of C–C bonds renders their cleavage a daunting challenge. To overcome this difficulty, several strategies, including the use of angle strain,2 a directing group,3,4 aromatization,4 and β-carbon elimination,5 have been successfully utilized to date. In contrast to nonpolar C–C bonds, polar C–C bonds, such as those in ketones, esters and nitriles, can be cleaved more readily by transition metals, although their bond dissociation energies are comparable to those for nonpolar C–C bonds.6 Regarding the metal-mediated cleavage of C[acyl]–C bonds in ketones, although most of the reported reactions continue to depend upon the use of angle strain2 or a directing group,1 several notable reactions that do not involve the use of such strategies have been reported. Murakami reported on a pioneering example of the metal-mediated activation of simple, unstrained ketones by developing the decarbonylation of cyclopentanones,7 while Brookhart later reported on rhodium-mediated decarbonylation of diaryl ketones.8 Our group previously reported that the decarbonylation of simple, unstrained ketones can also be mediated by a nickel/N-heterocyclic carbene (NHC) complex (Fig. 1a).9 Although these reactions are notable, in that neither ring strain nor a directing group is required to activate C–C bonds, it is necessary to use a stoichiometric amount of a metal complex. Catalytic C–C bond cleavage reactions of unstrained ketones have been reported to proceed when electronically activated ketones, such as diketones,10 acyl cyanides,11 alkynyl ketones,12 or ketones bearing a directing group13 are used (Fig. 1b). The catalytic C–C bond activation of simple ketones that proceed with the aid of a 2-aminopyridine cocatalyst, which serves as a temporary or removable directing group has been reported.14–16 Although these reactions demonstrate the power of transition metals for activating otherwise unreactive C–C bonds, the scope of the catalytic transformation of C–C bonds in ketones remains limited, compared with other unreactive bonds, including C–H bonds. We envisioned that 2,4,6-cycloheptatrien-1-one (tropone)17 derivatives would be suitable substrates for catalytic decarbonylation because the process involves the formation of a benzene ring which would be expected to drive the otherwise difficult C–C bond cleavage reaction. It should be noted that the decarbonylation of tropone was reported to require heating at over 600 °C (ref. 16a) or photoirradiation conditions (∼1% yield).16b Herein, we report on the development of a nickel/NHC complex that can catalyze the decarbonylation of tropone derivatives with the formation of a benzene ring (one-carbon ring contraction). In addition, the use of a bidentate ligand was found to allow for an unprecedented catalytic two-carbon ring contraction reaction of tropones, leading to the formation of cyclopentadiene derivatives (Fig. 1c).
Results and discussion

Catalytic decarbonylation reactions

We initiated our study by examining the decarbonylation of a series of tropone derivatives 1a–1d using Ni(cod)_2 (20 mol%) and IMesMe (20 mol%), which was used as an optimal catalyst in our previously reported nickel-mediated decarbonylation of simple ketones, in toluene at 160 °C for 18 h (Chart 1). No reaction occurred, however, and the starting ketones were recovered quantitatively under these conditions. Interestingly, the expected decarbonylation, in fact, proceeded, when a tropone bearing a fused phenanthrene ring (i.e., 1e) was used as a substrate, providing 2e in 93% yield. The 4,5-phenanthrene-fused tropones 1f and 1g bearing aryl substituents at α- and β-positions afforded the desired decarbonylated products 2f and 2g in a similar manner, whereas a tropone derivative lacking β-substituents, i.e., 1h, gave only a 6% yield. The acenaphthylene-fused analog 1i was decarbonylated successfully to furnish 2i in 97% yield.

Although tropones 1a–1i would all be expected to gain aromatic stabilization energy by decarbonylation, their reactivities toward the Ni/IMesMe catalyst were completely different. To obtain insights into structure/reactivity relationships, several structural and spectroscopic properties of the examined tropone derivatives were compared (Table 1). X-ray crystallographic analysis revealed that the Cα–C–O bond lengths of the successfully decarbonylated substrates 1e and 1i were relatively longer, and the bent angles of the tropone rings (θ and φ in Table 1) were larger than those for less reactive substrates 1c and 1h. All of these data suggest that the carbonyl groups in 1e and 1i are not conjugated with the π-system of the tropone ring in the solid state. 13C-NMR chemical shifts of the carbonyl carbons of 1e and 1i indicated that they were more deshielded than those of 1c and 1h, suggesting that 1e and 1i also behave as the non-conjugated ketones in solution. These bent structures found in 1e and 1i can be attributed to van der Waals (vdW) repulsion between the β-substituents and a large π-system fused to the tropone core. These analyses suggest that ground state destabilization by vdW strain is the key factor in

Table 1 ORTEP drawings, C–C and C–O bond lengths, and bent angles of tropone scaffolds

|   | 1c | 1h | 1e | 1i |
|---|----|----|----|----|
| Cα–C–O/Å | 1.48 | 1.49 | 1.51 | 1.51 |
| θ/deg. | ~0 | 51.6 | 57.5 | 62.1 |
| φ/deg. | ~0 | 28.4 | 43.2 | 32.8 |
| 13C-NMR (C–O)/ppm | 187 | 194 | 200 | 197 |

Note: θ and φ are the bent angles between the meanplanes (C2–C3–C6–C7 and C1–C2–C7) and (C2–C3–C6–C7 and C3–C4–C5–C6), respectively. Structural parameters for 1e (CCDC 2036614), 1h (CCDC 2100026) were abstracted from the Cambridge Structural Data Base.
promoting the C–C bond cleavage involved in this catalytic decarbonylation reaction of tropone derivatives.

To examine the catalyst turnover process, we next investigated the catalytic activity of Ni(CO)₃(IMesMe), which would be expected to be formed as the decarbonylation reaction proceeds (Scheme 1a). It was found that Ni(CO)₃(IMesMe) successfully catalyzed the decarbonylation of tropone 1e (94% yield). This result is in sharp contrast to the fact that this carbonyl complex does not catalyze the decarbonylation of simple ketones, which is the major reason for unsuccessful catalytic reactions. Therefore, the C(acyl)–C bond in 1e is more reactive than a corresponding bond of simple ketones because of vdW strain and can be activated by a less reactive CO-bound nickel species, allowing for a catalyst turnover. Indeed, the decarbonylation of 1e proceeded even at ambient temperature in 61% yield when a stoichiometric amount of a nickel complex was used (Scheme 1b), suggesting that a high temperature of 160 °C is required to release a CO ligand to regenerate an active Ni(0) species.

Catalytic two-carbon ring contraction reactions

During our optimization study of the decarbonylation of 1e, we envisioned that the use of a bidentate ligand would help to release a CO ligand from Ni(0) species, thereby improving the catalyst turnover step. Although these trials did not give satisfactory results for this decarbonylation, we noticed that a cyclopentadiene 3e was also formed in 8% yield, which appeared to be produced via the formal loss of CO and PhC units, when dcype was used as the ligand (Table 2, entry 1; Table S1, entry 6 in the ESI† for details), whereas no 3e was observed when NHCs or monodentate phosphine ligands, such as PCy₃, were used (Table S1,† entries 1–5 and 7). The unexpected formation of 3e led us to re-examine the reaction conditions with respect to the selective formation of 3e (Table 2). The generation of the decarbonylated product 2e was suppressed when the reaction was performed at 120 °C (entry 2). A brief screening of ligands and additives revealed that the use of other bidentate phosphines also gave the desired two-carbon elimination product 3e, although the highest yield was only 15% (entries 3–6). Considering that a hydrogen atom is incorporated during the formation of 3e, we subsequently examined the addition of a hydrogen source to the reaction mixture (entries 7–9). As a result, 3e was selectively formed quantitatively, when the nickel/dcype-catalyzed reaction of 1e was carried out in the presence of MeOH (10 equiv.) (entry 7). Importantly, under these conditions, PhCH₂CO₂Me was also formed (80% yield), suggesting that the rest of the fragment of 1e was eliminated as 2-phenylethen-1-one (phenylketene), which was trapped by the added MeOH. To the best of our knowledge, this reaction represents the first catalytic conversion of a tropone ring system into a five-membered ring skeleton.

To obtain insights into the mechanism responsible for the generation of 3e, a stoichiometric reaction of 1e, Ni(cod)₂, and dcye was performed in toluene at 100 °C, which led us to isolate the nickel–ketene complex 4e in 34% yield, along with 5e (56%) (Scheme 2a). The isolated ketene complex 4e was converted into the cyclopentadiene 3e in 84% yield by heating in toluene at 120 °C in the presence of EtOH (10 equiv.) (Scheme 2a)}
2b). In this reaction, PhCH$_2$CO$_2$Et was also formed in 76% yield, indicating that the ketene fragment in 4e is reductively cleaved$^{21}$ to give the cyclopentadiene 3e and a phenylketene, the latter of which was trapped by EtOH to form PhCH$_2$CO$_2$Et.

To collect additional mechanistic details for the conversion of the ketene complex 4e to cyclopentadiene 3e, we examined the Ni/dcape-catalyzed reaction of 1e with EtOH at lower temperature (Scheme 3a). As a result, when the reaction was carried out at 80 °C, the cyclobutanone derivative 6e was formed in 75% yield. This transformation is not a simple skeletal isomerization, but two additional hydrogen atoms were incorporated into 1e. The generation of 6e could be explained as follows. The C–C bond that connects a cyclopentadiene scaffold and a ketene moiety in complex 4e is reductively cleaved$^{4e,21,22}$ in the presence of EtOH to afford phenylketene (PhCH═C═O) and 3e, which subsequently undergoes a formal hetero [2 + 2] cycloaddition with the formation of the cyclobutanone 6e (Scheme 3a). Labelling experiments using EtOH-d$_6$ confirmed that the two hydrogen atoms that are incorporated into 6e are derived from EtOH (Scheme 3b). An independently synthesized nickel-free ketene 7e could be converted to 3e in a quantitative yield when a Ni/dcape catalyst was used (Scheme 3c). In contrast, 6e did not undergo C–C bond fission under thermal conditions, but rather the addition of EtOH to a ketene moiety occurred to form 8e in 33% yield (see Scheme 3f for the structure of 8e), suggesting that the nickel catalyst plays an active role in the C–C bond cleavage step. The reaction between PhCH═C═O and 3e proceeded thermally (in toluene at 80 °C for 72 h) to afford 6e in 63% yield (Scheme 3d). It is noteworthy that a thermal reaction between ketene and cyclopentadiene was reported to form cyclobutanone derivatives via a [4 + 2] reaction.
cycloadDITION/[3,3]-SIGMATROPIC rearrangement sequence, resulting in a net [2 + 2] cycloaddITION. **Cyclobutanone** 6e could be converted into 3e in 84% yield via a thermally-induced formal retro-[2 + 2] cycloaddITION reaction at 120 °C (Scheme 3e). Additional studies revealed that the use of 2,2'-bipyridine allows for the addition of EtOH to the ketene moiety of 7e, providing a new cyclopentadiene derivative 8e (Scheme 3f). This result further highlights the profound impact of the ligand on the course of these types of reactions.

On the basis of the mechanistic findings shown in Schemes 2 and 3, the nickel/dcype-mediated reaction of 1e can be summarized as depicted in Scheme 4. The isomerization of tropone 1e to the ketene complex 4e initially occurs at 80 °C. Subsequent nickel-mediated C–C bond cleavage occurs at 80 °C in the presence of EtOH with the formation of the cyclopentadiene 3e and phenylketene, which then undergo a thermally-induced formal [2 + 2] cycloaddITION to form cyclobutanone 6e. At higher temperatures, the reverse process from 6e to 3e begins to occur, leading to these compounds being in equilibrium. The phenylketene slowly and irreversibly reacts with EtOH at 120 °C (ref. 23) to form an ester (PhCH₂CO₂Et), thereby allowing for a selective formation of 3e at this temperature. Indeed, density functional theory (DFT) calculations at the M06-2X/6-31G(d,p) level of theory suggested that the sum of Gibbs free energies of 3e and PhCH₂CO₂Et is thermodynamically more stable than the sum of those for 6e and EtOH (ΔG = −25.9 kcal mol⁻¹).

**Computational studies**

Reaction mechanisms and ligand-controlled selectivity for both types of ring contraction reactions were also investigated by DFT calculations at the M06-2X/6-31G(d,p)-LanL2DZ level of theory (see ES† in details). The mechanism for the oxidative addition of a C–C bond was initially investigated when IMesMe was used as a ligand. The coordination of 1e to Ni(IMesMe) forms Int I, in which the C1–C2 bond of a phenyl group at the α-position coordinates in a η² manner, which is followed by the oxidative addition of a C1–C2 bond proceed via three-centred transition state TS I to give Int II. The activation barrier for this process is lower for 1e (11.7 kcal mol⁻¹) than that for unreactive substrates such as 1c (28.2 kcal mol⁻¹) and 1h (21.6 kcal mol⁻¹) (Fig. 2a). The results of a distortion/interaction analysis indicated that the distortion energy (ΔE‡strain) of Ni–IMesMe and 1e for TS I is smaller compared with that for 1c or 1h (see Table S2 in ES†). In contrast, the difference in the interaction energy (ΔE‡int) for these fragments for TS I is relatively small. The smaller ΔE‡strain of Ni–IMesMe and 1e indicates that 1e possesses a larger strain that originates from vdW repulsion between the bulky substituents compared to 1c or 1h, thereby leading to a lower activation barrier for this oxidative addition process. In contrast, when bidentate dctype is used as the ligand,
oxidative addition occurs from the $\eta^2$-(C=O) coordinated Ni(0)-dcype intermediate (i.e., Int I) via three-centred transition state TS I to generate INT II. The activation barrier for this oxidative addition is higher than that for Ni–IMesMe (15.0 kcal mol$^{-1}$) (Fig. 2b). The calculated activation barriers for oxidative addition of 1e are low for both IMesMe and dcype ligands, suggesting that the initial oxidative addition is not the rate-determining step of the decarbonylation reaction and high temperature is required for the dissociation of CO from Ni(0).

The ligand-controlled selectivity was next examined by exploring the reaction pathways after the oxidative addition complexes INT II/INT II' had been formed (Fig. 3). Using IMesMe as the ligand, INT II undergoes decarbonylation via INT III, in which the C6–C7 double bond of the nickelacycle coordinates to the nickel centre, with a reasonable activation barrier of 10.2 kcal mol$^{-1}$. The activation barrier for the competitive intramolecular insertion (ketene formation) process$^{25}$ is higher by 3.9 kcal mol$^{-1}$ compared to that for decarbonylation, thus rendering the decarbonylation pathway kinetically more favoured. When dcype is used as the ligand, INT II' is converted to INT III' by the coordination of an intramolecular alkene with one of the phosphorus atoms of dcype being dissociated. Although the difference in the activation barriers for the subsequent decarbonylation (i.e., the formation of INT IV) and ketene formation (i.e., the formation of INT V)$^{25}$ steps is less than 1 kcal mol$^{-1}$, the formation of INT V is exergonic, which explains the selective formation of cyclopentadiene in the case of a dcype ligand (Fig. 3).
Conclusions

In conclusion, we report on C–C bond cleavage reactions of tropone derivatives by nickel catalysis. When NHC is used as a ligand, the decarbonylation reaction proceeds catalytically to form a benzene ring (one-carbon ring contraction). In contrast, when dicye is used as the ligand, the tropone derivatives undergo a two-carbon ring contraction with the formation of cyclopentadiene derivatives. The addition of alcohol is essential for an efficient reaction, and the dissociated ketene fragment can be trapped by the cyclopentadiene moiety to generate polycyclic cyclobutanone derivatives. X-ray crystallography studies revealed that the formation of these compounds involves a nickel-ketene intermediate, which can be trapped by EtOH catalytically by changing the ligand from dicye to 2,2'-bipyridine. The judicious selection of the ligand and reaction temperature enables four different products, including three different ring systems, to be produced catalytically from a single substrate (Scheme 5).

Data availability

All experimental and characterization data are available in the ESI† Crystallographic data for compounds c1, i1, i4c, 5c, 6c, 8c, and Ni(CO)3(IMesMe) have been deposited in the Cambridge Crystallographic Data Centre under accession numbers CCDC 2115589–2115595.

Author contributions

T. K. and M. T. conceived the project. T. K. and K. S. performed the experimental work. T. K. and K. S. collected and analysed the spectroscopic data. T. K. and M. T. wrote the manuscript. All of the authors discussed the results and contributed to the preparation of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

1 Selected reviews: (a) M. Murakami, Cleavage of Carbon—Carbon Single Bonds by Transition Metals, in Activation of Unreactive Bonds and Organic Synthesis, Springer-Verlag Berlin Heidelberg, 1999, pp. 97–129; (b) F. Chen, T. Wang and N. Jiao, Chem. Rev., 2014, 114, 8613–8661; (c) C–C Bond Activation, ed. G. Dong, Springer-Verlag Berlin Heidelberg, 2014; (d) Cleavage of Carbon-Carbon Single Bonds by Transition Metals, ed. M. Murakami and N. Chatani, Wiley-VCH Verlag GmbH & Co. KGaA, 2015; (e) L. Souillard and N. Cramer, Chem. Rev., 2015, 115, 9410–9464; (f) M. Murakami and N. Ishida, J. Am. Chem. Soc., 2016, 138, 13759–13769; (g) P.-H. Chen, B. A. Billett, T. Tsukamoto and G. Dong, ACS Catal., 2017, 7, 1340–1360; (h) Z. Nairoukh, M. Cormier and I. Marek, Nat. Rev. Chem., 2017, 1, 0035; (i) F. Song, T. Gou, B.-Q. Wang and Z.-J. Shi, Chem. Soc. Rev., 2018, 47, 7078–7115; (j) L. Deng and G. Dong, Trends Chem., 2020, 2, 183–198; (k) H. Lu, T.-Y. Yu, P. F. Xu and H. Wei, Chem. Rev., 2021, 121, 365–411.

2 Selected reviews: (a) M. Rubin, M. Rubina and V. Georgyvan, Chem. Rev., 2007, 107, 3117–3179; (b) L. Jiao and Z.-X. Yu, J. Org. Chem., 2013, 78, 6842–6848; (c) T. Seiser, T. Saget, D. N. Tran and N. Cramer, Angew. Chem., Int. Ed., 2011, 50, 7740–7752; (d) P.-H. Chen and G. Dong, Chem.–Eur. J., 2016, 22, 18290–18315; (e) D. J. Mack and T. J. Njardarson, ACS Catal., 2013, 3, 272–286; (f) G. Fumagalli, S. Stanton and J. F. Bower, Chem. Rev., 2017, 117, 9404–9432; (g) R. Vicente, Chem. Rev., 2021, 121, 162–226.

3 Selected reviews: (a) Y. J. Park, J.-W. Parka and C.-H. Jun, Acc. Chem. Res., 2008, 41, 222–234; (b) D.-S. Kim, W.-J. Park and C.-H. Jun, Chem. Rev., 2017, 117, 8977–9015; (c) Y. Xia and G. Dong, Nat. Rev. Chem., 2020, 4, 600–614; Selected examples: (d) M. Gozln, A. Weisman, Y. Ben-David and D. Milstein, Nature, 1993, 364, 699–701; (e) J. Zhu, J. Wang and G. Dong, Nat. Chem., 2019, 11, 45–51; (f) S. Sakurai and M. Tobisu, Organometallics, 2019, 38, 2834–2838; (g) J. Zhu, R. Zhang and G. Dong, Nat. Chem., 2021, 13, 836–842.

4 (a) R. B. King and A. Efraty, J. Am. Chem. Soc., 1972, 94, 3773–3779; (b) R. H. Crabtree, R. P. Dion, D. J. Gibboni, D. V. Megrath and E. M. Holt, J. Am. Chem. Soc., 1986, 108, 7222–7227; (c) M. A. Halcroft, F. Urbanos and B. Chaudret, Organometallics, 1993, 12, 955–957; (d) S. W. Youn, B. S. Kim and A. R. Jagdale, J. Am. Chem. Soc., 2012, 134, 11308–11311; (e) G. Smits, B. Audic, M. D. Wodrich, C. Corminboeuf and N. Cramer, Chem. Sci., 2017, 8, 7174–7179; (f) Y. Xu, X. Qi, P. Zheng, C. C. Berti, P. Liu and G. Dong, Nature, 2019, 567, 373–378; Review; (g) F. Hu, L. Wang, L. Xu and S.-S. Li, Org. Chem. Front., 2020, 7, 1570–1575.

5 Selected reviews: (a) M. D. R. Lutz and B. Morandi, Chem. Rev., 2021, 121, 300–326; (b) K. Nogi and H. Yorimitsu, Chem. Rev., 2021, 121, 345–364.

6 Selected reviews: (a) M. Tobisu and N. Chatani, Chem. Soc. Rev., 2008, 37, 300–307; (b) M. Tobisu, Reactions via Cleavage of Carbon–Carbon Bonds of Ketones and Nitriles, in Cleavage of Carbon–Carbon Single Bonds by Transition Metals, Wiley-VCH Verlag GmbH & Co. KGaA, 2015, pp. 193–220; (c) Y. Nakao, Chem. Rev., 2021, 121, 327–344.

7 M. Murakami, H. Amii and Y. Ito, Nature, 1994, 370, 540–541.

8 O. Daugulis and M. Brookhart, Organometallics, 2004, 23, 527–534.

9 (a) T. Morioka, A. Nishizawa, T. Furukawa, M. Tobisu and N. Chatani, J. Am. Chem. Soc., 2017, 139, 1416–1419; Our group also reported on nickel-catalyzed decarbonylation of
amides and acylsilanes via C–C bond cleavage; (b) T. Morioka, S. Nakatani, Y. Sakamoto, T. Kodama, S. Ogoshi, N. Chetani and M. Tobisu, *Chem. Sci.*, 2019, 10, 6666–6671; (c) S. Nakatani, Y. Ito, S. Sakurai, T. Kodama and M. Tobisu, *J. Org. Chem.*, 2020, 85, 7588–7594.

10 K. Kaneda, H. Azuma, M. Wayaku and S. Tehanishi, *Chem. Lett.*, 1974, 3, 215–216.

11 (a) J. Blum, E. Oppenheimer and D. Bergmann, *J. Am. Chem. Soc.*, 1967, 89, 2338–2341; (b) S. Murahashi, T. Naota and N. Nakajima, *J. Org. Chem.*, 1986, 51, 898–901; (c) K. Nozaki, N. Sato and H. Takaya, *J. Org. Chem.*, 1994, 59, 2679–2681; (d) Y. Nishihara, Y. Inoue, M. Itazaki and K. Takagi, *Org. Lett.*, 2005, 7, 2639–2641; (e) Y. Kobayashi, H. Kamisaki, R. Yanada and Y. Takemoto, *Org. Lett.*, 2006, 8, 2711–2713; (f) Y. Nakao, Y. Hirata and T. Hiyama, *J. Am. Chem. Soc.*, 2006, 128, 7420–7421.

12 (a) A. Dermenci, R. E. Whittaker and G. Dong, *Org. Lett.*, 2013, 15, 2242–2245; (b) A. Dermenci, R. E. Whittaker, Y. Gao, F. A. Cruz, Z.-X. Yu and G. Dong, *Chem. Sci.*, 2015, 6, 3201–3210.

13 Selected examples: (a) N. Chatani, Y. Ie, F. Kakiuchi and S. Murai, *J. Am. Chem. Soc.*, 1999, 121, 8645–8646; (b) Z.-Q. Lei, H. Li, Y. Li, X.-S. Zhang, K. Chen, X. Wang, J. Sun and Z.-J. Shi, *Angew. Chem., Int. Ed.*, 2012, 51, 2690–2694; (c) R. Zeng and G. Dong, *J. Am. Chem. Soc.*, 2015, 137, 1408–1411; (d) R. Zeng, P. H. Chen and G. Dong, *ACS Catal.*, 2016, 6, 969–973; (e) Z.-Q. Lei, F. Pan, H. Li, Y. Li, X.-S. Zhang, K. Chen, X. Wang, Y.-X. Li, J. Sun and Z.-J. Shi, *J. Am. Chem. Soc.*, 2015, 137, 5012–5020; (f) C. Jiang, W.-Q. Wu, H. Lu, T.-Y. Yu, W.-H. Xu and H. Wei, *Asian J. Org. Chem.*, 2019, 8, 1358–1362; (g) C. Jiang, Z.-J. Zheng, T.-Y. Yu and H. Wei, *Org. Biomol. Chem.*, 2018, 16, 7174–7177; (h) T.-T. Zhao, W.-H. Xu, Z.-J. Zheng, P.-F. Xu and H. Wei, *J. Am. Chem. Soc.*, 2018, 140, 586–589; (i) T.-Y. Yu, W.-H. Xu, H. Lu and H. Wei, *Chem. Sci.*, 2020, 11, 12336–12340.

14 Selected examples: (a) C.-H. Jun and H. Lee, *J. Am. Chem. Soc.*, 1999, 121, 880–881; (b) Y. Xia, G. Lu, P. Liu and G. Dong, *Nature*, 2016, 539, 546–550; (c) J. Zhong, W. Zhou, X. Yan, Y. Xia, H. Xiang and X. Zhou, *Org. Lett.*, 2022, 24, 1372–1377.

15 Selected reviews on tropones, see: (a) P. L. Pauzon, *Chem. Rev.*, 1955, 55, 9–136; (b) F. Pietra, *Chem. Rev.*, 1973, 73, 293–364; (c) F. Pietra, *Acc. Chem. Res.*, 1979, 12, 132–138.

16 (a) T. Murai, T. Nakazawa and T. Shishido, *Tetrahedron Lett.*, 1967, 8, 2465–2469; (b) T. Murai and T. Sato, *Bull. Chem. Soc. Jpn.*, 1968, 41, 2819.

17 (a) T. Kodama, Y. Kawashima, Z. Deng and M. Tobisu, *Inorg. Chem.*, 2021, 60, 4332–4336; (b) T. Kodama, Y. Kawashima, K. Uchida, Z. Deng and M. Tobisu, *J. Org. Chem.*, 2021, 86, 13800–13807; A similar X-ray crystal structure of 1c was reported; see: (c) K. Ibata, H. Shimanouchi and Y. Sasada, *Acta Cryst.*, 1977, B33, 1129–1138.

18 A similar ground state destabilization by vdW strain is frequently utilized in the C–N bond activation of amides. A leading review: G. Meng, J. Zhang and M. Szostak, *Chem. Rev.*, 2021, 121, 12746–12783.

19 (a) The structure of 4e was unambiguously determined by X-ray crystallography (Fig. S8 in ESI†); (b) Related Ni/ketene complexes: N. D. Staudaher, A. M. Arif and J. Louie, *J. Am. Chem. Soc.*, 2016, 138, 14083–14091.

20 (a) S. Yamabe, T. Dai, T. Minato, T. Machiguchi and T. Hasegawa, *J. Am. Chem. Soc.*, 1996, 118, 6518–6519; (b) T. Machiguchi, T. Hasegawa, A. Ishiwata, S. Terashima, S. Yamabe and T. Minato, *J. Am. Chem. Soc.*, 1999, 121, 4771–4786.

21 Although the detailed mechanism responsible for this process is unclear, C–C bond cleavage is likely to be driven by aromatization (i.e., formation of cyclopentadienyl anion). See ref. 4a for a related reaction in this context.

22 The overall process is a reductive C–C bond cleavage, in which two hydrogen atoms are incorporated. The results of labelling studies confirmed that an external alcohol serves as the hydride source (Scheme 3b). β-Hydrogen elimination of metal–alkoxide species is presumably involved. For example, see: K. Yasui, M. Higashino, N. Chatani and M. Tobisu, *Synlett*, 2017, 28, 2569–2572.

23 The thermal reaction of PhCH=CH=O with EtOH in toluene was slower (19% at 80 °C; 59% at 120 °C for 72 h) than with the cyclopentadiene 3e (see ESI†), which is also consistent with the mechanistic scheme shown in Scheme 4.

24 F. M. Bickelhaupt and K. N. Houk, *Angew. Chem., Int. Ed.*, 2017, 56, 10070–10086.

25 The isomerization to a cyclopentadiene derivative is a concerted process that proceeds via TSIII/III in which C2 and C6 carbons are located close to facilitate the bond formation between these carbons.