Deprotonation of C-Alkyl Groups of Cationic Triruthenium Clusters Containing Cyclometalated C-Alkylpyrazinium Ligands: Experimental and Computational Studies

Javier A. Cabeza, José M. Fernández-Colinas, Pablo García-Álvarez, Enrique Pérez-Carreño, Vanessa Pruneda, and Juan F. Van der Maelen

Abstract: The C-alkyl groups of cationic triruthenium cluster complexes of the type [Ru₂(μ-H)(μ-κ²N,C⁻L)(CO)₁₀] (HL represents a generic C-alkyl-N-methylpyrazinium) have been deprotonated to give kinetic products that contain unprecedented C-alkylidene derivatives and maintain the original edge-bridged decacarbonyl structure. When the starting complexes contain various C-alkyl groups, the selectivity of these deprotonation reactions is related to the atomic charges of the alkyl H atoms (as suggested by DFT-NBO calculations). Three additional electronic properties of the C-alkyl C–H bonds have also been found to correlate with the experimental regioselectivity, since, in all cases, the deprotonated C–H bond is that having the smallest electron density at the bond critical point, the greatest Laplacian of the electron density at the bond critical point, and the greatest total energy density ratio at the bond critical point (QTAIM calculations). The kinetic decacarbonyl products evolve, under appropriate reaction conditions that depend upon the position of the C-alkylidene group in the heterocyclic ring, toward face-capped nonacarbonyl derivatives (thermodynamic products). The position of the C-alkylidene group in the heterocyclic ring determines the distribution of single and double bonds within the ligand ring and this strongly affects the stability of the neutral decacarbonyl complexes and the way these ligands coordinate to the metal atoms in the nonacarbonyl products. The mechanisms of these decacarbonylation processes have been investigated by DFT methods, which have rationalized the structures observed for the final products and have shed light on the different kinetic and thermodynamic stabilities of the reaction intermediates, explaining the reaction conditions experimentally required by each transformation.

Keywords: C–H deprotonation • cationic ligands • N-ligands • pyrazinium ligands • C–H activation

Introduction

Metal complexes containing cationic ligands derived from aromatic six-membered-ring N-heterocycles can be classified in two broad groups according to the atom through which the ligand is attached to the metal: a) those having a C-metalated “inium” ligand and b) those containing an N-metalated “inium” ligand. The first group comprises mononuclear and trinuclear complexes that generally derive from N-substituted pyridines¹-² ⁴ or other one-N⁻² ⁴ or two-N³ heterocycles, but their ligands are best described as neutral N-heterocyclic carbenes (Figure 1, A). The complexes of the second group are mostly mononuclear, they contain an N-substituted N’-coordinated two-N heterocycle, and are well represented in the literature, particularly for N-methylpyrazinium, which is a very strong π-acceptor ligand (Figure 1, B). A few reports dealing with their one-electron-reduction to mononuclear radical derivatives have been published, but ligand deprotonation processes have not been hitherto reported.

![Figure 1](https://example.com/fig1.png)

Figure 1. “Carbene” and “inium” resonance structures of a C-metalated pyridinium (A) and an N-metalated pyrazinium (B) in cationic metal complexes.

Complexes that can concurrently be ascribed to both groups (a and b), i.e., those derived from C- and N-metalated “inium” cations, were unknown before the recent description of the cationic triruthenium derivatives [Ru₂(μ-H)(μ-κ²N,C⁻L)(CO)₁₀]¹, HL = N-methylquinolinium, N-methylpyrazinium, N-methylpyrimidinium, 1,2-dimethylpyrimidinium and 1-methyl-1,5-naphthyridinium. The cationic ligands of these triruthenium clusters are readily attacked by anionic nucleophiles at selected C atoms of their ligand rings (some examples are...
depicted in Scheme 1)\(^\text{[7-9]}\) and are also prone to undergo one-electron-reduction processes that lead to dimeric hexanuclear products\(^\text{[8-10]}\). These nucleophilic attacks and reduction reactions are orbital-controlled rather than charge-controlled processes and lead to neutral complexes with unsaturated but nonaromatic N-heterocyclic ligands that in some cases are N-heterocyclic carbenes (Scheme 1).

![Scheme 1](image)

This paper reports that the alkyl groups of triruthenium clusters containing C-alkylpyrazinum-derived ligands can be selectively deprotonated to give neutral products that contain novel C-alkylidenepyrazine-derived ligands\(^\text{[11]}\). Theoretical studies (DFT-NBO atomic charges and QTAIM analysis of the electron density) have been used to rationalize the regioselectivity of deprotonation reactions of starting materials containing various C-alkyl groups on different positions of the pyrazine ring. DFT analysis of potential energy surfaces has been used to shed light on the mechanisms of observed decarbonylation processes, including that of an unexpected and very interesting transformation of a decacarbonyl complex having a methylidene group on the C\(^2\) carbon atom of the pyrazine ring into a derivative that formally has that methylidene group on the C\(^3\) carbon atom of the pyrazine ring.

C-Alkyl deprotonation is unprecedented for C-alkylpyrazinum metal complexes. Although it has been observed for metal-free C-alkylpyrazinum cations,\(^\text{[12,13]}\) the corresponding deprotonated products, which are useful intermediates in heterocyclic syntheses,\(^\text{[12]}\) are not stable enough to be isolated.

**Results and Discussion**

**Synthesis of the cationic cluster precursors:** The cationic C-alkylated triruthenium clusters used in this work (compounds 1b–5b, Scheme 2) were prepared from [Ru\(_2\)(CO)\(_2\)]\(_2\), the corresponding C-alkylpyrazine, and methyl triflate, following the synthetic procedure previously used to prepare [Ru\(_2\)(μ-H)(μ-κ\(^2\)N,C-L)(CO)\(_3\)]OTf (HL = N-methylquinolinium).\(^\text{[7]}\) The experimental details of these reactions and the spectroscopic and other analytical data of their products are given in the Supporting Information.

![Scheme 2](image)

The reactions of compounds 1b, 2b, 4b, and 5b with K[N(SiMe\(_3\))] proceeded quickly in THF at room temperature to give the respective C\(^2\)-alkylidene nonacarbonyl derivatives 1c, 2c, 4c, and 5c (Scheme 3), as major components of reaction mixtures that also contained small amounts of the N-demethylated clusters 1a, 2a, 4a, or 5a, respectively. All these reaction products were satisfactorily separated by chromatographic techniques and were characterized by spectroscopic and analytical methods, and, in the case of compounds 2e and 4e (Figure 2), also by X-ray diffraction.

All the C\(^2\)-alkylidene derivatives have a common IR v(CO) pattern and a hydride NMR resonance at ca. \(-14.0\) ppm, confirming that they all have an analogous molecular structure. Their +FAB mass spectra are also in agreement with their nonacarbonyl structures. The stereochemistry of the ethylidene group of compound 5c was established by NOE \(^1\)H NMR, which clearly indicated that the N–Me group is closer to the C=CH proton than to the C=CMe protons, which, in turn, are in the vicinity of the C\(^6\)–H ring proton (Figure S4 of Supporting Information).
The C=aryl group of the cationic pyrimidine-derived complex [Ru(u-H)(μ-η^2,N,C-pyrMe_2)(CO)]^+ (HpyrMe_2 = 1,2-dimethylpyrimidinium) can also be deprotonated with a strong base,\(^{19}\) that reaction is the only previously reported deprotonation related to those described in this paper.

We were surprised by the unique reactivity of compound 3b (in comparison with the remaining reactions shown in Scheme 3), founding the different reactivities of 3b and 4b particularly intriguing because both compounds have methyl substituents at either sides (C1 and C5 positions) of the N=Me group, differing only by the absence (3b) or presence (4b) of a methyl group on the ring C6 carbon atom. These different reactivities imply a) a different regioselectivity of the deprotonation processes, i.e., deprotonation of the C1=Me group of 3b but deprotonation of the C5=Me group of 4b, and b) a different stability of the deprotonated decacarbonyl products, since that arising from 3b is stable at room temperature (compound 3c, Scheme 3) whereas that arising from 4b is unstable under similar conditions, evolving toward the observed nonacarbonyl product 4c (Scheme 3). These regioselectivity issues are addressed in the following sections of this manuscript.
Table 1. QTAIM topological parameters for the C–H bonds of 1b<sup>−</sup>–5b<sup>−</sup>, calculated at the B3P86/WTBS/6-311++G(3df,3pd) level of theory.

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<th>Cluster</th>
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<th>(\rho_b [\text{e} \text{ Å}^{-3}]^{[5]})</th>
<th>(V^2\rho_b [\text{e} \text{ Å}^{-5}]^{[4]})</th>
<th>(H_b/\rho_b \text{ [h c}^{-1}]^{[7]})</th>
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<sup>[7]</sup>Electron density at the bcp (smallest value of each complex underlined).  <sup>[8]</sup>Laplacian of the electron density at the bcp (smallest absolute value of each complex underlined).  
<sup>[9]</sup>Total energy density ratio at the bcp (smallest absolute value of each complex underlined).  
<sup>[10]</sup>Kinetic energy density ratio at the bcp.  

As occurs with the NBO charges, the differences between the QTAIM data of the ligand C–H bonds of each cluster are not large enough to solely justify the presence of only one product in the deprotonation reactions. Therefore, these reactions should also be influenced by factors that have not been included in the computations such as cation-anion interactions, solvent effects, etc.

**Themolysis of compound 3c. Experimental and theoretical studies:** With the aim to address the higher stability of compound 3c (it is stable at room temperature) in comparison with those of the related decacarbonyl species that are the primary products of the deprotonation of compounds 1a, 2a, 4a and 5a (they evolve to the corresponding nonacarbonyl derivatives at subambient temperature),...
temperatures; Schemes 3 and 4), we studied the thermolysis of 3c both experimentally and by theoretical calculations.

The heating of compound 3c in THF at 50 °C slowly (it took ca. 8 h to observe the complete disappearance of the starting cluster) led to a ca. 1:5 mixture of the noncarbonyl derivatives 3d and 3e (Scheme 5). The reaction was performed in a Schlenk tube, initially under a nitrogen atmosphere, closed by a silicone bubbler. The final ratio of the reaction products and the reaction time depended on the number of times the system was opened (with nitrogen purge of the gas phase) to monitor the reaction (by IR and/or TLC). A reaction monitored by 1H NMR revealed that 3d was the first compound formed, but, while the amount of 3e increased with the reaction time, that of 3d remained nearly constant until the end of the reaction. Compound 3d could not be isolated free of 3e. The treatment of this mixture with CO (gas bubbled) reformed compound 3e.

\[
\text{Scheme 5. Thermolysis of compound 3e.}
\]

![Scheme 5](image)

Figure 5. 1H NMR (CDCl₃, 293 K, 400 MHz) in the positive ppm region of compound 3e (top) and 1D NOE-difference spectra after saturation at the frequencies of the inverted signals.

The 1H NMR shift of the hydride of compound 3d (~17.14 ppm) is comparable to that of [Ru₃(μ-H)(μ-κ²N,C-pyMe)(CO)] (pyMe = N-methylpyridin-2-ylidene) and other similarly bridged noncarbonyl triruthenium clusters. In addition, the 1H NMR shift of the hydride of compound 3e (~13.90 ppm) and its IR νCO absorption pattern are comparable to those of 1c, 2c, 4c, 5c. These data confirm that the ligand arrangements around the Ru₃ cores of compounds 3d and 3e are those shown in Scheme 5. The location of the methylidene group in each cluster was established by NOE 1H NMR. Figure 5 unequivocally demonstrates that the C=CH₂ group of 3e, which is observed as a singlet at 4.50 ppm, is close to both the N-Me group and the C₆-H proton, while the latter is far away from the C-Me group.

Therefore, while the reaction that gives 3d from 3e is a simple decarbonylation process, the reaction that leads to 3e also implies a surprising rearrangement that “apparently” involves a hydrogen shift from the C₆-methyl group to the C₆-methylene group.

To explain these results, the mechanisms of the reactions 3c → 3d + CO and 3e → 3e + CO were theoretically investigated by exploring their associated potential energy surfaces in the gas phase. These calculations were carried out by DFT methods at the B3LYP/LanL2DZ/6-31G(d,p) level of theory.

Figure 6 shows that the reaction 3c → 3d + CO is an elemental process that implies the displacement of an axial CO ligand from the Ru(CO)₅ fragment of 3e by the metallated C=N double bond of the bridging ligand. The calculated energy barrier of this process, 23.9 kcal mol⁻¹, is not low enough to be easily accessible at room temperature but is easily reachable at 50 °C. As the energy of the reaction products (3d + CO) is higher than that of 3e, the amount of 3e in the equilibrium should be larger than that of 3d if CO is not evacuated from the system.

![Figure 6](image)

Figure 6. DFT-calculated mechanism for the transformation of 3e into 3d + CO. The given energies (ΔE, kcal mol⁻¹) are relative to that of 3e.

Figures 7 and 8 display a calculated mechanism that accounts for the transformation of 3c into 3e + CO. The first step (Figure 7) is a reductive elimination process, which engages the hydride and the metallated carbon atom of the bridging ligand and converts complex 3e into a coordinatively unsaturated intermediate having a terminally bound pyrazinium-type ligand (11). A 180° rotation of this ligand about the Ru–N bond places the original C₆–H hydrogen atom in close proximity to the unsaturated Ru atom (12). A subsequent orthometalation (oxidative addition) of this bond leads to intermediate 3j, whose ligand arrangement is analogous to 3c but has the methylidene group in position 5 of the ligand ring. This implies that 3e and 3j also have a different distribution of double and single bonds in their corresponding ligand ring, e.g., the N¹ and C² atoms are connected through a double bond in 3c (N¹=C² 1.35 Å) but through a single bond in 3j (N¹=C² 1.40 Å), and this fact accounts for their different energies (3j is 6.5 kcal mol⁻¹ less stable than 3e). The barrier to the isomerization of 3c into 3e (37.1 kcal mol⁻¹) is also accessible at 50 °C but is 13.2 kcal mol⁻¹ higher than that of the transformation of 3c into 3d + CO (Figure 8). This explains the experimental fact that compound 3d is the first product observed during the thermolysis of 3c.
The approach of the C² carbon atom of intermediate i3 toward the Ru(CO)₄ fragment provokes a terminal-to-bridging rearrangement of one of its CO ligands (ts5, Figure 8) that induces the release of the CO ligand that is trans to the bridging CO and cis to the hydride in ts5. In the resulting intermediate, i4, the heterocyclic ligand caps the Ru₃ triangle. Although the energy of i4 + CO is higher than that of i3, the energy barrier of this step is small (18.8 kcal mol⁻¹) and the transformation of i4 into the final product 3e (in two steps that imply a CO rearrangement and a ca. 60° rotation of the capping ligand over the Ru₃ triangle) is kinetically (low activation barrier) and thermodynamically favored (3e is 4.4 kcal mol⁻¹ more stable than i4). In addition, the evacuation of CO from the reaction system stimulates the transformation of i3 into 3e.

We also found a mechanism for a direct transformation of 3d into 3e (not implicating 3c), but various steps of such a reaction pathway have much higher activation barriers than those involved in the mechanisms shown in Figures 6–8. Consequently, we do not believe that 3d be an intermediate in the transformation of 3c into 3e + CO.

The mechanism shown in Figure 8 also explains why no decacarbonyl C⁵-alkylidene intermediates were observed when the deprotonations of 1b, 2b, 4b and 5b, which undergo deprotonation at their C⁵-alkyl group, were carried out at room temperature (Scheme 3), but they were detected in reactions performed at lower temperature before ending in the final nonacarbonyl products 1e, 2c, 4e and 5c, respectively, when the temperature was raised (Scheme 4). As these decacarbonyl C⁵-alkylidene intermediates should be structurally similar to intermediate i3 (they all have the alkylidene group in position 5 of the ligand ring and have the same distribution of single and double bonds within the ring), they should easily release CO (irreversibly in an unsealed system) to give the corresponding nonacarbonyl derivatives.

Conclusions

This manuscript demonstrates that the C-alkyl groups of cationic triruthenium cluster complexes containing ligands derived from C-alkyl N-methylpyridinium can be deprotonated to give unprecedented C-alkylidene derivatives.

Theoretical calculations support the proposal that, when the starting complexes contain various C-alkyl groups, the selectivity of these deprotonation reactions is primarily determined by the atomic charge of the alkyl H atoms, the higher the charge the easier the deprotonation. Three additional electronic properties of the C-alkyl C–H bonds have also been found to be related to the experimental regioselectivity, since, for each starting complex, the deprotonated C–H bond is that having the smallest electron density at the bond critical point, the greatest Laplacian of the electron density at the bond critical point, and the greatest total energy density ratio at the bond critical point. This type of calculations may be useful for researches interested in the reactivity of C–H bonds.
It has been established that the distribution of single and double bonds within the heterocyclic ligands of the deprotonated products (C-alkylidylenederivatives) determines affects the stability of the decarboxylation intermediates (kinetic products) and also the structures (the coordination of the ligand to the metal atoms) of the final noncarboxyl complexes (thermodynamic products). Thus, while the edge-bridged decarboxyl derivative 3e, which has a C₂-methylidene group, is isolable at room temperature, the related decarboxyl C₂-alkylidene derivatives are unstable at room temperature, evolving toward the corresponding face-capped noncarboxyl products 1c, 2c, 4c and 5c. Two face-capped noncarboxyl products, 3d and 3e, have been isolated after heating compound 3e in THF at 50 °C. While 3d maintains the original C-methylidene group in position 3 of its heterocyclic ligand, the methylidene group of 3e is in position 5.

The mechanisms by which the edge-bridged C-alkylidylenederacarboxyl (kinetic) products are transformed into the corresponding noncarboxyl derivatives (thermodynamic products) have been investigated by DFT methods. These studies have rationalized not only the structures of the final products but also have shed light on the kinetic and thermodynamic stability of the reaction intermediates, explaining the reaction conditions experimentally required by each transformation.

In addition, this work opens up the possibility of extending the deprotonation C-alkyl-N-heterocyclic ligands to mononuclear complexes and also gives the initial step toward the functionalization of such ligands via C-alkylidylenederivatives, processes that have not been hitherto investigated.

Experimental Section

General: Solvents were dried over Na[PhCHO] (THF, diethyl ether, hydrocarbons) or CaH₂ (dichromethane) and were distilled under nitrogen prior to use. The reactions were carried out under nitrogen, using Schlenk-vacuum line techniques, and were routinely monitored by solution IR spectroscopy and by spot TLC on silica gel. All reagents were purchased from commercial sources. All reaction products were vacuum-dried for several hours prior to being weighed and analyzed. IR: Perkin-Elmer FT Paragon 1000X. NMR: Bruker AV-400, AV-300, NMR-400, and DPX-300, room temperature (r.t.), residual solvent as internal standard. Microanalyses: Perkin-Elmer 2400B. MS: VG Autospec double-focusing mass spectrometer operating in the FAB+ mode; ions were produced with a standard Cs⁺ gun at about 30 kV; 3-nitrobenzyl alcohol was used as matrix; data given correspond to the most abundant molecular ion isotope. The experimental details of the syntheses of compounds 1a-5a and 1b-5b (Scheme 2) and their spectroscopic and other analytical data are given in the Supporting Information.

[Ru(µ-µ(C)(µ-C)(µ-C)=Me-5-C)=CH₂(C)(CO)(CN)₂] (1c): A toluene solution of K[N(SiMe₃)₂] (155 mL, 0.5 M, 0.178 mmol) was dropwise added to a suspension of compound 1b (150 mg, 0.178 mmol) in THF (30 mL) at -80 °C. The color changed from red to brown. The system was warmed up to room temperature and the solid was filtered off. An aliquot of the resulting solution was analyzed by H NMR. The spectrum showed the presence of a mixture that comprised 1a (17%), 1e (48%), and smaller amounts of unidentified hydroxy-containing products. All attempts to obtain pure 1e by chromatographic methods (TLC and silica or alumina columns) were unsuccessful. 1H NMR (CDCl₃, r.t., ppm): δ 8.75 (2 H, 1 H, CH), 6.49 (1 H, 1 H, CH), 4.33 (d, J = 3.2 Hz, 1 H, CH), 4.45 (d, J = 3.2 Hz, 1 H, CH), 3.08 (3 H, NCH₃), 14.56 (1 H, µ-H); 13C[¹H] NMR (CDCl₃, r.t., ppm): δ 199.3, 195.9 (CO)s, 166.6 (CH), 151.7 (CH), 137.0 (C), 101.7 (C), 96.2 (CH₂), 40.8 (CCH₃). 1H NMR (CDCl₃, r.t., ppm): δ 8.74 (µ-C)(µ-C)=Me-5-C)=CH₂(C)(CO)(CN)₂] (2c): A toluene solution of K[N(SiMe₃)₂] (175 mL, 0.5 M, 0.088 mmol) was dropwise added to a suspension of compound 2b (75 mg, 0.088 mmol) in THF (30 mL) at -80 °C. The color changed from orange to brown. The system was warmed up to room temperature and the solid was filtered off. An aliquot of the resulting solution was analyzed by H NMR. The spectrum showed the presence of a mixture of 2a (5%) and 2e (95%). The solvent was removed under reduced pressure, the residue was extracted into dichloromethane (1.5 mL), and this solution was placed onto an alumina column (2 x 10 cm, activity IV) packed in hexane. Hexane eluted a trace amount of [Ru₂(CO)₆]³⁺. Hexane-dichloromethane (4:1) eluted compound 2c, which was isolated as an orange solid (50 mg, 84%). Analysis (%) found (calcd) for C₂₀H₁₂N₄O₃Ru₂: C 28.41 (28.37); H 1.58 (1.58); N 4.05 (4.14). IR (CHCl₃, cm⁻¹): ν(CO) (2070) 2039, 2039 (vs), 2018 (m), 1990 (m), 1975 (w), 1954 (w). The ν(CO) peaks of the starting material were observed at 1990 (w), 1975 (w), 1954 (w). The ν(CO) peaks of the starting material were observed at 1990 (w), 1975 (w), 1954 (w). The ν(CO) peaks of the starting material were observed at 1990 (w), 1975 (w), 1954 (w). The ν(CO) peaks of the starting material were observed at 1990 (w), 1975 (w), 1954 (w).

Thermolysis of 3c: A THF solution (20 mL) of compound 3c (20 mg, 0.028 mmol) was stirred at 50 °C for 7.5 h. The color changed from red to dark orange. An aliquot of the resulting solution was analyzed by H NMR. The spectrum showed the presence of a mixture of 3c (15%), 3d (15%), and 3e (70%). The solvent was removed under reduced pressure, the residue was extracted into dichloromethane (1.5 mL), and this solution was placed onto a silica gel column (2 x 10 cm) packed in hexane. Hexane eluted a red band containing a mixture of unidentified compounds. Hexane-dichloromethane (4:1) eluted a mixture of unidentified compounds. The mixture was fractionated, and the compounds were collected in order of elution, compounds 3c (11 mg, 60%) and 3d. The last product could not be completely separated from some 3e. Data for 3d: H NMR (CDCl₃, r.t., ppm): δ 5.88 (s, 1 H, CH₂), 4.46 (d, J = 2.1 Hz, 1 H, CH₃), 4.17 (d, J = 2.1 Hz, 1 H, CH₃), 2.87
Cartesian coordinates for the atoms of all optimized structures are given in positive eigenvalues) or transition states functional.

Isotropic and full matrix anisotropic least square refinements were carried out using SHELXL. All non-H atoms were refined anisotropically. The position of the hydride atom of 2e was calculated with XHDFD.EX.

Theoretical calculations: DFT computations (using the Gaussian09 program package22) of NBO charges23 and QTAIM topological parameters (using the AIM2000 program24) were performed by using the B3P86 hybrid functional.25 The large all-electron 6-311+G(d,p) basis set was employed for C, H, N, and O atoms, while the large all-electron WBTS (“Well-Tempered Basis Set”) of Huzinaga and co-workers26 basis set was used for the Ru atoms. Structure optimizations and mechanistic DFT calculations were carried out using the hybrid B3LYP functional.27 The Lanz2D basis set, with relativistic effective core potentials, was used for the Ru atom and the remaining atoms were treated with 31G(d,p). All optimized stationary points were confirmed as energy minima (all positive eigenvalues) or transition states (one imaginary eigenvalue) by analytical calculation of frequencies. IRC calculations were used to verify the transition states found were correct saddle points connecting the proposed minima. All energies given in this contribution are potential energies calculated in gas phase. All mechanistic calculations were carried out with the Gaussian09 program package.22 Cartesian coordinates for the atoms of all optimized structures are given in the Supporting Information.

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Deprotonation of C-Alkyl Groups of Cationic Triruthenium Clusters Containing Cyclometalated C-Alkylpyrazinium Ligands: Experimental and Computational Studies

Reactive alkyl groups: On triruthenium clusters, the C-methyl or C-ethyl groups of N,C-dimetalated C-alkylpyrazinium ligands can be selectively deprotonated by K[N(SiMe₃)₂], through charge-controlled processes, to give neutral products that contain a C-alkylidene group on the heterocyclic ring. DFT and QTAIM calculations have shed light on the regioselectivity of these reactions.