www.angewandte.org

Sandwich Complexes

 How to cite: Angew. Chem. Int. Ed. 2022, 61, e202211555

 International Edition:
 doi.org/10.1002/anie.202211555

 German Edition:
 doi.org/10.1002/ange.202211555

Isolation and Characterization of the Homoleptic Nickel(I) and Nickel(II) Bis-benzene Sandwich Cations

Manuel Schmitt, Maximilian Mayländer, Tim Heizmann, Sabine Richert, Christine Bülow, Konstantin Hirsch, Vicente Zamudio-Bayer, J. Tobias Lau, and Ingo Krossing*

Abstract: A stable salt of the metalloradical $[Ni(C_6H_6)_2]^+$ hitherto unknown in the condensed phase was synthesized from $[Ni(CO)_4]^+[WCA]^-$ and benzene $([WCA]^-=[F\{Al(OR^F)_3]_2]^-; R^F=C(CF_3)_3)$. Single crystal XRD reveals a remarkable asymmetrically η^3, η^6 -slipped sandwich structure. The magnetic properties of the $[Ni(C_6H_6)_2]^+$ cation were determined in solution and in the gas phase. Oxidation with the synergistic Ag⁺/ 0.5 l₂ system led to the salt $[Ni(C_6H_6)_2]^{2+}([WCA]^-)_2$. All products were fully characterized by means of IR, Raman, NMR/EPR, single crystal and powder XRD.

With the discovery of $Cr(C_6H_6)_2$, the first transition metal (TM) sandwich complex of neutral arenes,^[1] a fascinating field opened in 1955 that soon led to entries for most of the early TMs in group 4 to 9 as well as the coinage metals Ag and $Cu.^{[2]}$ However, cationic sandwich complexes $[M(C_6H_6)_2]^{m+}$ with the prototypical benzene as ligand are rarer and hitherto only structurally characterized for $M = V,^{[3]} Cr,^{[4]} Mo,^{[5]} Tc,^{[6]} Re,^{[7]} Co,^{[8]} Ru,^{[9]} and Ag.^{[10]} Almost all$

[*] M. Schmitt, T. Heizmann, Prof. Dr. I. Krossing Institut für Anorganische und Analytische Chemie and Freiburger Materialforschungszentrum (FMF), Albert-Ludwigs-Universität Freiburg Albertstr. 21, 79104 Freiburg (Germany) E-mail: krossing@uni-freiburg.de M. Mayländer, Dr. S. Richert Institut für Physikalische Chemie, Albert-Ludwigs-Universität Freiburg Albertstr. 21, 79104 Freiburg (Germany) Dr. K. Hirsch, Dr. V. Zamudio-Bayer Abteilung für Hochempfindliche Röntgenspektroskopie, Helmholtz-Zentrum Berlin für Materialien und Energie Albert-Einstein-Straße 15, 12489 Berlin (Germany) Dr. C. Bülow, Prof. J. T. Lau Abteilung für Hochempfindliche Röntgenspektroskopie, Helmholtz-Zentrum Berlin für Materialien und Energie Albert-Einstein-Straße 15, 12489 Berlin (Germany) and Physikalisches Institut, Universität Freiburg Hermann-Herder-Straße 3, 79104 Freiburg (Germany) 🕤 © 2022 The Authors. Angewandte Chemie International Edition published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution Non-Commercial

the terms of the Creative Commons Attribution Non-Commercial License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes. of these sandwich complexes exhibit a η^6 -coordination of the benzene ligands to the metal. Only the Ag^+ complex shows a η^2 -coordination. A similar observation was made by Duncan et al. during a systematic investigation of the 3d $[M(C_6H_6)_2]^+$ complexes by IR photodissociation spectroscopy in the gas phase and supported by DFT calculations.^[11] Overall, η^6 -coordination is expected for the early 3d TMs, whereas for the late TMs (Ni, Cu) a slipped sandwich structure is anticipated.^[11] To investigate these unusual late TM slipped sandwich complexes, we focused on the isolation and characterization of $[Ni(C_6H_6)_2]^+$ in the gas and condensed phase.

Ni^I complexes are still less common than their Ni⁰ or Ni^{II} analogues, especially ionic and monomeric ones.[12,13] However, the number of known Ni^I compounds has rapidly grown over the last decade due to their use in catalysis,^[12,13] small molecule activation^[14,15] and biological systems.^[12,15] Yet, only few examples of Ni^I complexes containing neutral with NHC,^[16] arenes together β-diketiminate,^[17] guanidinato,^[18] and phosphine^[19] ligands and only one salt $[Ni(NO)Mes][PF_6]^{[20]}$ are known (Mes=1,3,5-Me₃C₆H₃). In addition, earlier attempts to prepare [Ni(arene)₂]⁺ salts by reactions of excess arenes (C6H6, Mes, C6Me6) with $[Ni(cod)_2][Al(OR^F)_4]$ only led to the 19 valence electron (VE) complex salts $[Ni(cod)(arene)]^+[Al(OR^F)_4]^{-[21]}$ and homoleptic Ni^I arene complexes were not accessible. By contrast, they are well-known in the gas phase and were studied by mass spectrometry^[11,22-27] and theoretical investigations,^[28–31] yielding data,[11,22] IR bond dissociation^[23,27] and ionization energies.^[24,25] Magnetic measurements were hitherto not reported.

Turning to divalent homoleptic [Ni^{II}(arene)₂]²⁺ salts, Fischer and Lindner reported 1968 on the isolation of $[Ni(C_6Me_6)_2][PtX_6]$ (X=Cl,Br),^[32] but without structure. Only one publication by Green et al.^[33] from 2000 reports on the isolation of an $[Ni(C_6H_6)_2]^{2+}$ salt in the condensed phase of nickelocene with bv reaction $[H(OEt_2)_2]$ $[B(3,5-(CF_3)_2C_6H_3)_4]$ (Brookhart's acid) in benzene. However, upon closer inspection of the reported crystal structure, the $[Ni(C_6H_6)_2]^{2+}$ cation contains exceptionally short C-C bond lengths with values as low as 0.98(2) Å, which indicates that the cation may be disordered $[Ni(C_5H_5)_2]^+$ instead (see Supporting Information section 6 for a detailed discussion). Our attempts to reproduce the results by Green et al. with a perfluoroalkoxy aluminate anion always yielded a mixture of $[Ni(C_5H_5)(C_5H_6)][Al(OR^F)_4]$ and $[Ni(C_5H_5)_2]$ - $[Al(OR^{F})_{4}]$ (Supporting Information section 6.1). Hence, it appeared interesting to revisit the $[Ni(C_6H_6)_2]^{2+}$ cation using

Angew. Chem. Int. Ed. 2022, 61, e202211555 (1 of 5)

© 2022 The Authors. Angewandte Chemie International Edition published by Wiley-VCH GmbH

a different route. Here, we report on the synthesis and characterization of the homoleptic Ni^I and Ni^{II} benzene cations $[Ni(C_6H_6)_2]^{+/2+}$ in the condensed phase and the measurements of the isolated $[Ni(C_6H_6)_2]^+$ cation in the gas phase (X-ray magnetic circular dichroism spectroscopy (XMCD) and X-ray absorption spectroscopy (XAS)).

For the synthesis of other Ni^I complexes, the recently reported [Ni(CO)₄][F{Al(OR^F)₃]₂]^[34] is an excellent starting material, as the CO ligands can be displaced rather easily. In agreement, the calculated energetics for the formation of amount to $\Delta_{\rm R}G^{\circ}/\Delta_{\rm R}H^{\circ} = -59/$ gaseous $[Ni(C_6H_6)_2]^+$ $+26 \ kJ \ mol^{-1} \quad at \quad the \quad DLPNO\text{-}CCSD(T)/def2\text{-}QZVPP//$ B3LYP(D3BJ)/def2-TZVPP level of theory. Hence, $[Ni(C_6H_6)_2][F{Al(OR^F)_3}_2]$ **1a** was prepared by addition of an excess of benzene to a solution of [Ni(CO)₄][F{Al- $(OR^{F})_{3}_{2}$ in 1,2,3,4-tetrafluorobenzene (4FB) and slow removal of the solvent under reduced pressure [Eq. (1)]. By vapor diffusion of n-pentane into a 4FB/benzene solution, light yellow crystals of **1a** were obtained (crystalline yield: 61 %). Note that for the clean synthesis of $[Ni(CO)_4]^+$ and $[Ni(C_6H_6)_2]^+$, the use of the stable and very weakly coordinating anion $[F{Al(OR^F)_3}_2]^{-[35]}$ is essential. Although the corresponding $[Ni(C_6H_6)_2][Al(OR^F)_4]$ 1b can be obtained by the same procedure with the less stable [Al-(OR^F)₄]⁻ anion,^[36] this is always accompanied by partial decomposition of the anion (Supporting Information section 4.2). On one occasion, orange crystals of the decomposition product $[Ni(C_6H_6)_2][Ni_2(OR^F)_2]F_2Al(OR^F)_2][FAl(OR^F)_3]_2]$ 1c were

obtained. With the strong synergistic $Ag^+/0.5 l_2$ system,^[37,38] which was necessary for the synthesis of the carbonyl radical cations $[Ni(CO)_4]^{+[34]}$ and $[M(CO)_6]^+$ (M=Mo,W),^[39] **1a** was further oxidized in 4FB to $[Ni(C_6H_6)_2][F{Al(OR^F)_3}_2]_2$ [Eq. (2)].

$$\begin{bmatrix} [Ni(CO)_4]^+ & +2 C_6 H_6 / -4 CO \\ [WCA]^- & 4FB \\ \Delta_r G^{\circ}_{(g)} = -59 \text{ kJ/mol} \\ \Delta_r H^{\circ}_{(n)} = +26 \text{ kJ/mol} \end{bmatrix} \begin{bmatrix} [WCA]^- & 1a \\ 1 \end{bmatrix}$$
(1)

$$[WCA]^{-} = [F\{AI(OR^{F})_{3}\}_{2}]^{-}$$

$$[Ni(C_{6}H_{6})_{2}]^{+} + \underline{Ag[WCA]} + 0.5 I_{2} [Ni(C_{6}H_{6})_{2}]^{2+}$$
(2)
$$[WCA]^{-} 1a - \underline{AgI} / 4FB ([WCA]^{-})_{2} 2$$

Yellow crystals of **2** were obtained by vapor diffusion of *n*-pentane into the reaction solution (crystalline yield: 40%). Although **2** can be obtained by oxidation of **1a** with Ag⁺ without the addition of I₂, these reactions always yielded significant amounts of $[Ag(C_6H_6)_2][F{Al(OR^F)_3}_2]$ **3** as a side product. **3** was also intentionally produced by addition of benzene to Ag[F{Al(OR^F)_3}_2] in 4FB and used as reference to determine the effective magnetic moment of **1a** and **2** in solution. **1a**, **2** and **3** were fully characterized by means of single crystal XRD, NMR/EPR, IR, Raman, and bulk purity was proven with powder XRD (Supporting Information). All obtained compounds are sensitive to moisture and air

but are stable at room temperature for multiple days without noticeable decomposition.

The molecular structure of the cation in 1a is displayed in Figure 1a.^[40] The nickel atom in **1a** is remarkably asymmetrically coordinated by the two benzene ligands. The three shortest Ni–C bond lengths of the η^3 -bound benzene ligand vary between 2.152(4) Å and 2.362(3) Å, whereas the other three Ni-C distances are significantly longer and range from 2.681(4) Å to 2.914(3) Å. By contrast, the Ni–C distances of the second η^6 -bound benzene ligand are more evenly distributed between 2.133(4) Å and 2.418(3) Å, resulting in the η^3 , η^6 -slipped sandwich structure of the cation. Similar cation structures were observed for 1b and 1c, although the individual bond lengths vary (see Supporting Information section 5.1, Table S3 and S4). The variation in bond lengths and the partial (17%) disorder of the nickel atom in the plane between the benzenes in 1a (Figure S14) demonstrates that the structure exhibits some flexibility. The flat potential energy hypersurface with respect to the torsion of the benzene ligands also represents a challenge for any geometry optimization in DFT calculations. Depending on the employed DFT functional, different minimum structures of the $[Ni(C_6H_6)_2]^+$ cation were found. With the B3LYP functional, Hase et al.^[30] obtained a η^3 , η^4 -slipped sandwich structure, although also a η^3 , η^3 -structure was reported with the B3LYP^[11,22] or M11L^[31] functional. A η^3, η^6 -structure was predicted by Duncan et al. with the BPW91-D2 method, which they verified by comparison with experimental gas phase IR data in the C-H region.^[22,28] To compare the different structures, we performed single point DLPNO-CCSD(T)/def2-QZVPP calculations on the minimum structures obtained using four DFT functionals (BP86, B3LYP, pbeh-3c and TPSSh). The energetically lowest optimized structure was the η^3 , η^6 -structure obtained with the TPSSh functional, which matches the experimental structure and bond lengths well (Supporting Information section 13).

Additional experimental evidence for an asymmetric sandwich structure of the free, cryogenically cooled cation $[Ni(C_6H_6)_2]^+$ (g) was obtained from the comparison of measured and simulated carbon K-edge X-ray absorption spectra (Supporting Information, section 7). While no agreement is observed for the η^6, η^6 -structure, the comparison shows good agreement with simulated spectra of asymmetric structures with reduced hapticity.

Furthermore, the gas-phase effective magnetic moment of $2.32 \pm 0.10 \,\mu_{\rm B}$ for the free cation, $[{\rm Ni}({\rm C_6H_6})_2]^+$ (g), from X-ray magnetic circular dichroism spectroscopy (XMCD) in a cryogenic ion trap (see Supporting Information section 8), is larger than the spin-only value of the expected doublet state of $\mu_{\rm spin} = 1.73 \,\mu_{\rm B}$ due to a considerable orbital magnetic moment contribution. A separate determination of the spin and orbital magnetic moments of $[{\rm Ni}({\rm C_6H_6})_2]^+$ (g), as possible by XMCD,^[41] reveals a considerable orbital contribution to $\mu_{\rm eff}$ of $0.59 \pm 0.10 \,\mu_{\rm B}$. The orbital contribution to the magnetic moments is also persistent in the condensed phase. In solution, a slightly lower effective magnetic moment compared to the gas-phase of $2.02 \pm 0.05 \,\mu_{\rm B}$ was determined for **1a** in 4FB using Evans NMR method (Supporting Information section 9).^[42,43] 5213773, 2022, 50, Downloaded from https://onlinelibrary.viley.com/doi/10.1002/anie.202211555 by Helmholtz-Zentrum Berlin Für, Wiley Online Library on [06/12/2022]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

Angewandte

Chemie

Communications



Figure 1. a) Top and side view of the $[Ni(C_6H_6)_2]^+$ cation in the crystal structure of **1** a $(P\bar{1}, R_1 = 4.9\%, wR_2 = 10.3\%, disorder of the nickel atom not shown).^[40] b) Top and side view of the <math>[Ni(C_6H_6)_2]^{2+}$ dication in the crystal structure of **2** $(P\bar{1}, R_1 = 4.2\%, wR_2 = 11.0\%)$. Thermal ellipsoids are shown at the 50% probability level.^[40] c) Measured and simulated X-band continuous wave EPR spectrum of solid **1** a at 100 K. The feature marked with an asterisk may be caused by a potential unknown impurity. The **g**-tensor obtained by numerical simulation of the experimental spectrum is shown together with calculated values and the calculated spin density (cutoff: 0.02 a.u., B3LYP/EPR-II(6-31G* for Ni)). d) Cyclic voltammogram (100 mV s⁻¹) of **1** a (10 mM) in 4FB with an external Fc[Al(OR^F)₄]/Fc (10 mM) reference electrode and [NBu₄][Al(OR^F)₄] (100 mM) as conducting salt (see Supporting Information section 10).

The X-band continuous wave EPR spectrum of solid **1a** at 100 K (Figure 1c) shows a rhombic **g**-tensor of **g**=(2.066, 2.076, 2.587), which qualitatively agrees with the calculated values of **g**=(2.120, 2.184, 2.533) (@B3LYP/EPR-II (6-31G* for Ni)). The calculated spin density is mainly located at the nickel atom and only to a very minor extent on the η^3 -bound benzene ligand.

In addition to the vibrational bands in the C–H region, two other bands at 1469 cm^{-1[11]} and 732 cm^{-1[11]} where observed in the gas phase IR spectrum of the $[Ni(C_6H_6)_2]^+$ cation by Duncan et al. and assigned to the in-plane carbon ring distortion and out-of-plane C–H bend, respectively.^[11] In the IR spectrum of **1a** (Figure S39), only one vibrational band of the cation at 1463 cm⁻¹ was observed, as the other one overlaps with an anion band at 727 cm⁻¹. The bands in the C–H region were not observed, probably due to their low intensity as supported by DFT calculations (Figure S39). However, C–H vibrational bands were observed in the Raman spectrum of **1a** (Figure S40) at 3108 cm⁻¹ and 3066 cm⁻¹ together with the symmetrical ring breathing mode at 978 cm⁻¹.

The cyclic voltammogram of **1a** in 4FB (Figure 1d) reveals one irreversible reduction of $[Ni(C_6H_6)_2]^+$ to $[Ni(C_6H_6)_2]^0$ with an cathodic peak potential of 0.39 V vs. Fc⁺/Fc and one reversible redox process with a half wave potential of 1.19 V vs. Fc⁺/Fc, which can be assigned to the $[Ni(C_6H_6)_2]^{2+}/[Ni(C_6H_6)_2]^+$ couple. The neutral $[Ni(C_6H_6)_2]^0$ is not stable under these conditions at RT and subsequent decomposition to elemental nickel occurs, which was

observed as a black solid on the platinum disc working electrode after the measurement.

Chemical oxidation of **1a** with the $Ag^+/0.5 l_2$ system,^[37,38] as described above, yields the $[Ni(C_6H_6)_2]^{2+}$ dication. The dication has 20 VE, a triplet ground state and is isoelectronic to the earlier reported $[Co(C_6H_6)_2]^{+,[8]}$ The crystal structure of the dication in **2** is shown in Figure 1b and displays an ecliptic η^6, η^6 -sandwich structure with Ni–C bond lengths in the narrow range of 2.248(2) Å to 2.269(2) Å.^[40] Similar to the monocation, the $[Ni(C_6H_6)_2]^{2+}$ dication shows a flat potential energy hypersurface at the B3LYP(D3BJ)/def2-TZVPP level of theory in respect to the torsion of the benzene ligands and we found both an ecliptic η^6, η^6 sandwich structure (torsion angle 0°) and a staggered η^6, η^6 sandwich structure (29°) as local minima with very similar energies (Supporting Information section 13).

The in-plane carbon ring distortion mode in the IR spectrum of **2** at 1466 cm⁻¹ (Figure S43) and the symmetric ring breathing mode in the Raman spectrum at 983 cm⁻¹ (Figure S44) are only blue-shifted by 3 cm⁻¹ and 5 cm⁻¹ compared to **1a**. No C–H bands could be observed in the IR spectrum of **2**, which is probably caused by their low intensity as they were also very weak in the IR spectrum of $[Co(C_6H_6)_2][Al(OR^F)_4]$.^[8] The effective magnetic moment of **2** in 4FB determined with Evans method^[42,43] amounts to $2.76\pm0.04 \mu_B$, which agrees with the spin-only expectation value (2.83 μ_B) of the triplet ground state of **2** (Supporting Information section 9).

To conclude, the $[Ni(CO)_4]^+$ in combination with the stable $[F{Al(OR^F)_3}_2]^-$ anion proved as an excellent starting material for the synthesis of novel ionic Ni^I compounds in the condensed phase. This method should likely be transferable to other weak ligands for potential application in Ni^I catalysis. As a textbook example, the synthesis of the $[Ni(C_6H_6)_2]^+$ cation is described, which displays a remarkable asymmetric η^3, η^6 -slipped sandwich structure. Additionally, the 20VE $[Ni(C_6H_6)_2]^{2+}$ dication is accessible by oxidation with the synergistic Ag⁺/0.5 l₂ system.

Acknowledgements

The authors would like to thank Dr. H. Scherer and F. Bitgül for NMR measurements, Dr. T. Ludwig for pXRD measurements, Dr. B. Butschke for help with scXRD measurements and Dr. V. Radtke for help with cyclic voltammetry. This work was funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation)-Project numbers 350173756 (I.K.), 417643975 (S.R.). The authors acknowledge support by the state of Baden-Württemberg through bwHPC and the German Research Foundation (DFG) through grant no INST 40/575-1 FUGG (JUSTUS2 cluster). Beamtime for this project was granted at the Ion Trap endstation of BESSY II, beamline UE52-PGM, operated by Helmholtz-Zentrum Berlin. This project has received funding from the German Federal Ministry of Education and Research through Grant No. BMBF-05K16VF1. Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Arene Ligands • Nickel • Sandwich Complexes • Transition Metals • Weakly Coordinating Anion (WCA)

- [1] E. O. Fischer, W. Hafner, Z. Naturforsch. 1955, 10, 665-668.
- [2] G. Pampaloni, Coord. Chem. Rev. 2010, 254, 402–419.
- [3] R. Choukroun, C. Lorber, L. Vendier, *Organometallics* 2007, 26, 3604–3606.
- [4] a) B. Morosin, Acta Crystallogr. Sect. B 1974, 30, 838–839;
 b) A. Fischer, J. Organomet. Chem. 1996, 525, 291–294.
- [5] D. O'Hare, M. Kurmoo, R. Lewis, H. Powell, J. Chem. Soc. Dalton Trans. 1992, 1351–1355.
- [6] M. Benz, H. Braband, P. Schmutz, J. Halter, R. Alberto, *Chem. Sci.* 2015, 6, 165–169.
- [7] E. A. Trifonova, D. S. Perekalin, K. A. Lyssenko, A. R. Kudinov, J. Organomet. Chem. 2013, 727, 60–63.

- [8] S. C. Meier, A. Holz, J. Kulenkampff, A. Schmidt, D. Kratzert, D. Himmel, D. Schmitz, E.-W. Scheidt, W. Scherer, C. Bülow et al., Angew. Chem. Int. Ed. 2018, 57, 9310–9314; Angew. Chem. 2018, 130, 9454–9458.
- [9] U. Beck, W. Hummel, H. B. Buergi, A. Ludi, *Organometallics* 1987, 6, 20–22.
- [10] a) M. F. Ibad, A. Schulz, A. Villinger, Organometallics 2019, 38, 1445–1458; b) C. Jenne, B. Wegener, Z. Anorg. Allg. Chem. 2018, 644, 1123–1132.
- [11] T. D. Jaeger, D. van Heijnsbergen, S. J. Klippenstein, G. von Helden, G. Meijer, M. A. Duncan, J. Am. Chem. Soc. 2004, 126, 10981–10991.
- [12] C.-Y. Lin, P. P. Power, Chem. Soc. Rev. 2017, 46, 5347–5399.
- [13] A. Bismuto, P. Finkelstein, P. Müller, B. Morandi, *Helv. Chim. Acta* 2021, 104, e2100182.
- [14] a) S. Yao, M. Driess, Acc. Chem. Res. 2012, 45, 276–287;
 b) M. T. Kieber-Emmons, C. G. Riordan, Acc. Chem. Res. 2007, 40, 618–625.
- [15] P. Zimmermann, C. Limberg, J. Am. Chem. Soc. 2017, 139, 4233–4242.
- [16] W. J. M. Blackaby, S. Sabater, R. C. Poulten, M. J. Page, A. Folli, V. Krewald, M. F. Mahon, D. M. Murphy, E. Richards, M. K. Whittlesey, *Dalton Trans.* **2018**, *47*, 769–782.
- [17] S. Pfirrmann, S. Yao, B. Ziemer, R. Stösser, M. Driess, C. Limberg, Organometallics 2009, 28, 6855–6860.
- [18] C. Jones, C. Schulten, L. Fohlmeister, A. Stasch, K. S. Murray, B. Moubaraki, S. Kohl, M. Z. Ertem, L. Gagliardi, C. J. Cramer, *Chem. Eur. J.* 2011, 17, 1294–1303.
- [19] a) A. Bismuto, P. Müller, P. Finkelstein, N. Trapp, G. Jeschke,
 B. Morandi, J. Am. Chem. Soc. 2021, 143, 10642–10648;
 b) D. E. Herbert, N. C. Lara, T. Agapie, Chem. Eur. J. 2013, 19, 16453–16460;
 c) R. Beck, S. A. Johnson, Organometallics 2013, 32, 2944–2951.
- [20] A. M. Wright, G. Wu, T. W. Hayton, *Inorg. Chem.* 2011, 50, 11746–11753.
- [21] a) M. M. Schwab, D. Himmel, S. Kacprzak, D. Kratzert, V. Radtke, P. Weis, K. Ray, E.-W. Scheidt, W. Scherer, B. de Bruin et al., *Angew. Chem. Int. Ed.* **2015**, *54*, 14706–14709; *Angew. Chem.* **2015**, *127*, 14919–14922; b) M. M. Schwab, D. Himmel, S. Kacprzak, Z. Yassine, D. Kratzert, C. Felbek, S. Weber, I. Krossing, *Eur. J. Inorg. Chem.* **2019**, 3309–3317.
- [22] T. D. Jaeger, M. A. Duncan, J. Phys. Chem. A 2005, 109, 3311– 3317.
- [23] M. M. Kappes, R. H. Staley, J. Am. Chem. Soc. 1982, 104, 1813–1819.
- [24] T. Kurikawa, H. Takeda, A. Nakajima, K. Kaya, Z. Phys. D 1997, 40, 65–69.
- [25] T. Kurikawa, H. Takeda, M. Hirano, K. Judai, T. Arita, S. Nagao, A. Nakajima, K. Kaya, *Organometallics* 1999, 18, 1430– 1438.
- [26] W. Zheng, J. M. Nilles, O. C. Thomas, K. H. Bowen, J. Chem. Phys. 2005, 122, 044306.
- [27] F. Meyer, F. A. Khan, P. B. Armentrout, J. Am. Chem. Soc. 1995, 117, 9740–9748.
- [28] M. Castro, R. Flores, M. A. Duncan, J. Phys. Chem. A 2013, 117, 12546–12559.
- [29] a) Ç. A. Demircan, U. Bozkaya, J. Phys. Chem. A 2017, 121, 6500–6509; b) B. K. Rao, P. Jena, J. Chem. Phys. 2002, 117, 5234–5239; c) I. S. Youn, D. Y. Kim, N. J. Singh, S. W. Park, J. Youn, K. S. Kim, J. Chem. Theory Comput. 2012, 8, 99–105; d) G. E. Froudakis, A. N. Andriotis, M. Menon, Chem. Phys. Lett. 2001, 350, 393–398.
- [30] B. Kerkeni, A. J. A. Aquino, M. R. Berman, W. L. Hase, *Mol. Phys.* 2019, 117, 1392–1403.
- [31] R. Flores, M. Castro, J. Mol. Struct. 2016, 1125, 47-62.
- [32] H. H. Lindner, E. O. Fischer, J. Organomet. Chem. 1968, 12, P18–P20.

 \odot 2022 The Authors. Angewandte Chemie International Edition published by Wiley-VCH GmbH

- [33] J. L. Priego, L. H. Doerrer, L. H. Rees, M. L. H. Green, *Chem. Commun.* 2000, 779–780.
- [34] M. Schmitt, M. Mayländer, J. Goost, S. Richert, I. Krossing, Angew. Chem. Int. Ed. 2021, 60, 14800–14805; Angew. Chem. 2021, 133, 14926–14931.
- [35] A. Martens, P. Weis, M. C. Krummer, M. Kreuzer, A. Meierhöfer, S. C. Meier, J. Bohnenberger, H. Scherer, I. Riddlestone, I. Krossing, *Chem. Sci.* 2018, 9, 7058–7068.
- [36] I. M. Riddlestone, A. Kraft, J. Schaefer, I. Krossing, Angew. Chem. Int. Ed. 2018, 57, 13982–14024; Angew. Chem. 2018, 130, 14178–14221.
- [37] P. J. Malinowski, D. Himmel, I. Krossing, Angew. Chem. Int. Ed. 2016, 55, 9262–9266; Angew. Chem. 2016, 128, 9408–9412.
- [38] P. J. Malinowski, D. Himmel, I. Krossing, Angew. Chem. Int. Ed. 2016, 55, 9259–9261; Angew. Chem. 2016, 128, 9405–9407.
- [39] J. Bohnenberger, M. Schmitt, W. Feuerstein, I. Krummenacher, B. Butschke, J. Czajka, P. J. Malinowski, F. Breher, I. Krossing, *Chem. Sci.* 2020, 11, 3592–3603.
- [40] Deposition Numbers 2175301 (for 1a), 2175302 (for 1b), 2175303 (for 1c), 2175304 (for 2), 2175305 (for 3) and 2175306

(for $[Ni(C_5H_5)(C_5H_6)][Al(OR^F)_4]$) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

- [41] a) M. Niemeyer, K. Hirsch, V. Zamudio-Bayer, A. Langenberg, M. Vogel, M. Kossick, C. Ebrecht, K. Egashira, A. Terasaki, T. Möller et al., *Phys. Rev. Lett.* 2012, *108*, 57201;
 b) S. T. Akin, V. Zamudio-Bayer, K. Duanmu, G. Leistner, K. Hirsch, C. Bülow, A. Ławicki, A. Terasaki, B. von Issendorff, D. G. Truhlar et al., *J. Phys. Chem. Lett.* 2016, *7*, 4568–4575.
- [42] D. F. Evans, J. Chem. Soc. 1959, 2003–2005.
 [43] S. K. Sur, J. Magn. Reson. 1989, 82, 169–173.
- [45] S. K. Sul, J. Mugh. Resol. 1969, 62, 109–17.

Manuscript received: August 5, 2022

Accepted manuscript online: October 5, 2022

Version of record online: October 5, 2022