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How to cite: *Angew. Chem. Int. Ed.* **2021**, *60*, 14800–14805

International Edition: doi.org/10.1002/anie.202102216

German Edition: doi.org/10.1002/ange.202102216

Chasing the Mond Cation: Synthesis and Characterization of the Homoleptic Nickel Tetracarbonyl Cation and its Tricarbonyl-Nitrosyl Analogue

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Dedicated to Professor Wolfgang Kaim on the occasion of his 70th birthday

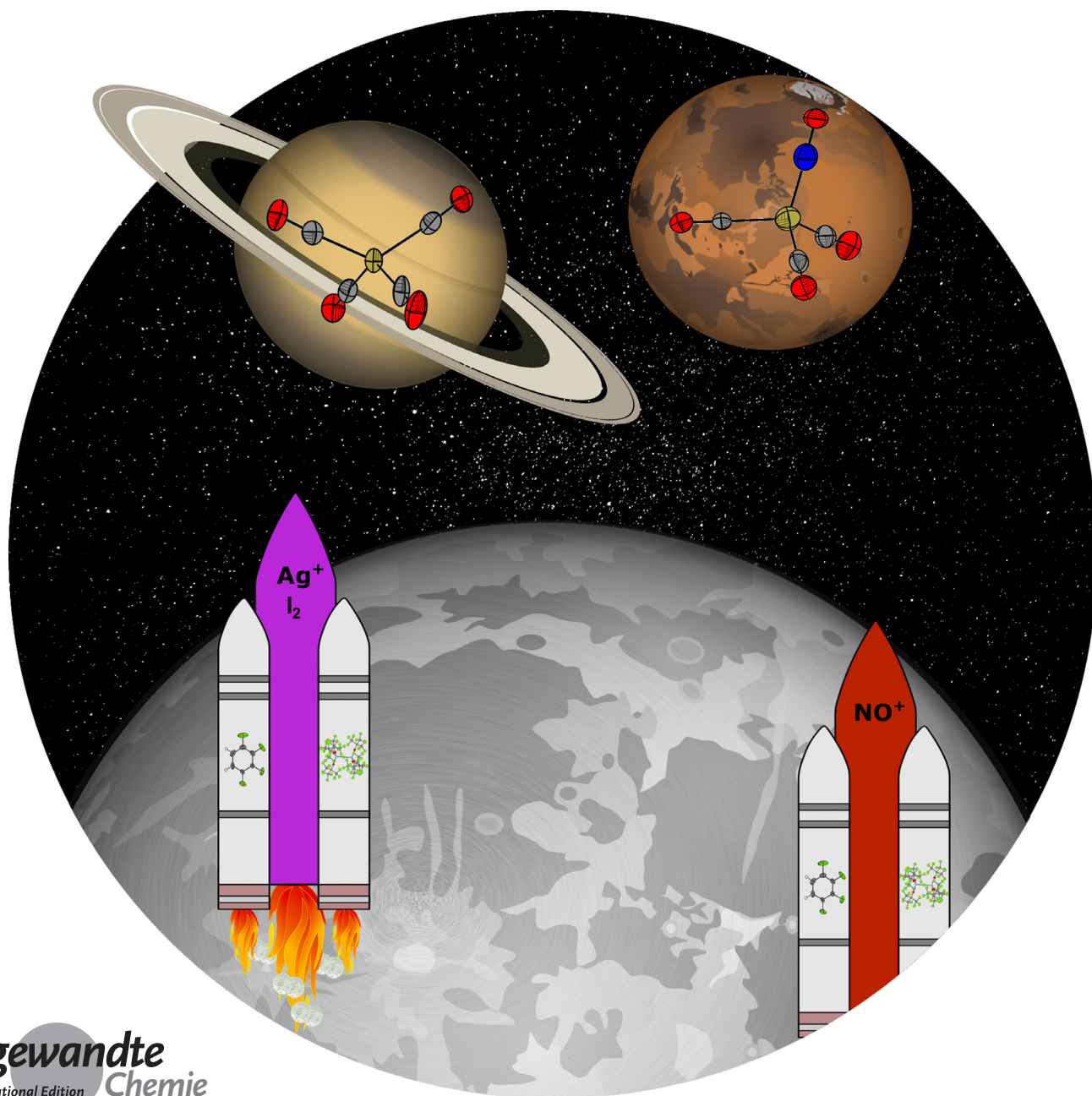


Table 1: Hitherto structurally characterized mononuclear homoleptic transition metal carbonyl cations.^[a]

	3	4	5	6	7	8	9	10	11	12
3d	Sc*	Ti*	V*	[Cr(CO) ₆] ^{+ [23]}	[Mn(CO) ₆] ^{+ [24]}	[Fe(CO) ₆] ²⁺	[Co(CO) ₅] ⁺	Ni*	[Cu(CO) _{1.4}] ^{+ [25]}	Zn
4d	Y*	Zr*	[Nb(CO) ₇] ^{+ [26]}	[Mo(CO) ₆] ^{+ [20]}	[Tc(CO) ₆] ⁺	[Ru(CO) ₆] ^{2+ [27]}	[Rh(CO) ₄] ^{+ [b]}	[Pd(CO) ₄] ^{2+ [b]}	[Ag(CO) _{1.2}] ⁺	Cd
5d	La*	Hf*	[Ta(CO) ₇] ^{+ [26]}	[W(CO) ₆] ^{+ [20]}	[Re(CO) ₆] ⁺	[Os(CO) ₆] ^{2+ [27]}	[Ir(CO) ₄] ^{+ [b]}	[Pt(CO) ₄] ^{2+ [b]}	[Au(CO) ₂] ⁺	[Hg(CO) ₂] ²⁺

[a] TMCCs were only cited when the reference to the crystal structure is not included with the reviews.^[5,9,13,22] [b] 16 VE species. Note: TMCCs of metals indicated by * were only spectroscopically characterized in the gas phase by mass-selected infrared laser photodissociation spectroscopy or in noble gas matrices. To the best of our knowledge, none of them were hitherto isolated in the condensed phase.

products **1** and **2** were fully characterized by means of IR, Raman, NMR/EPR and single crystal XRD and bulk purity was proven with powder XRD and EDX.

In the crystal structure of **1**, the NO ligand is disordered over multiple positions (Supporting Information, Section 6)^[54] and the cation [Ni(CO)₃(NO)]⁺ almost appears *T_d* symmetric, like the isoelectronic Ni(CO)₄. The expected difference in the mean Ni-C/N bond lengths between the products **1** (1.847(9) Å) and **2** (1.931(5) Å) agrees with the calculated values for [Ni(CO)₃(NO)]⁺ (1.872 Å) and [Ni(CO)₄]⁺ (1.975 Å) (@B3LYP(D3BJ)/def2-TZVPP). The NO stretch in **1** resonates at 1953 cm⁻¹, while the CO frequencies

are significantly blue-shifted (2202 cm⁻¹ (*A₁*), 2182 cm⁻¹ (*E*); Figure 1a).^[36,37] The NO ligand is visible in the ¹⁴N NMR spectrum at 4.9 ppm (Supporting Information, Figure S4). Product **1** is isomorphous and isoelectronic to earlier reported [Mn(NO)₄]^{+ [39]} and [Fe(CO)(NO)₃]^{+ [31]} salts. Their almost linear M-C-O/M-N-O units (176 to 179°) are described in terms of the Enemark–Feltham notation^[40] as [MNO]¹⁰.

The assignment of oxidation states in nitrosyl complexes is not trivial due the covalent character of the metal nitrosyl bond as published by Klüfers et al.^[41] With CASSCF calculations and the effective-oxidation-state method^[42] they assigned the π-bonding M-NO electrons. Yet, due to the

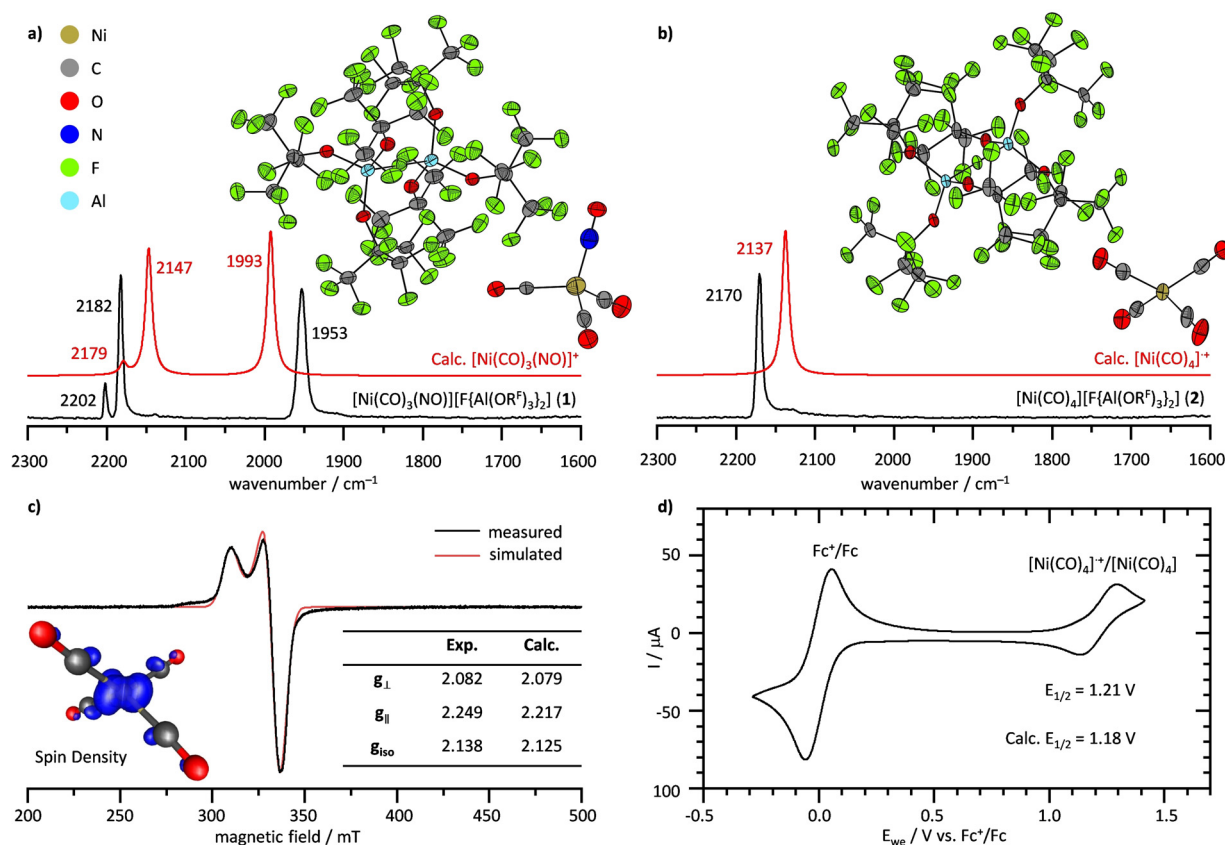


Figure 1. a),b) One formula unit of the crystal structure of **1** (*P* $\bar{1}$, *R*₁ = 6.1 %, *wR*₂ = 12.4 %)^[54] and **2** (*P* $\bar{1}$, *R*₁ = 6.5 %, *wR*₂ = 16.1 %)^[54] together with the corresponding experimental and simulated IR spectra (calculated at BP86(D3BJ)/def2-TZVPP level without scaling factor). c) Measured and simulated X-band continuous wave EPR spectrum of solid **2** at 100 K. The *g*-values obtained by numerical simulation of the experimental spectrum are shown together with calculated values and the calculated spin density (cutoff: 0.005 a.u., B3LYP/EPR-II(6-31G* for Ni)). d) Cyclic voltammogram (100 mV s⁻¹) of **2** (10 mM) in **4FB** with Fc[Al(OR^F)₄] (10 mM) as internal reference and [NBu₄][Al(OR^F)₄] (100 mM) as conducting salt together with the calculated half wave potential (@B3LYP(D3BJ)/def2-TZVPP, solvent correction with the COSMO-RS^[45] model, see the Supporting Information, Section 11).

Table 2: Comparison of the experimental data of **1** and **2** with Ni(CO)₄ and the corresponding calculated values.

	1	calcd [Ni(CO) ₃ (NO)] ⁺ (C _{3v}) ^[a]	2	calcd [Ni(CO) ₄] ⁺ (D _{2d}) ^[a]	Exp. Ni(CO) ₄	calcd Ni(CO) ₄ (T _d) ^[a]
IR $\tilde{\nu}$ (CO/NO) [cm ⁻¹]	1953 (w) 2182 (w) 2202 (vw)	1993 (100), ν (NO), A ₁ 2147 (88), ν_{as} (CO), E 2179 (8), ν_s (CO), A ₁	2170 (w)	2137 (100), ν_{as} (CO), E 2139 (24), ν_{as} (CO), B ₂	2057 (vs.) ^[46]	2038 (100), ν_{as} (CO), T ₂
Raman $\tilde{\nu}$ (CO/NO) [cm ⁻¹]	1955 (w) 2184 (vs.) 2202 (s)	1993 (3), ν (NO), A ₁ 2147 (19), ν_{as} (CO), E 2179 (20), ν_s (CO), A ₁	2174 ^[b] 2201 ^[b]	2137 (38), ν_{as} (CO), E 2139 (54), ν_{as} (CO), B ₂ 2175 (37), ν_s (CO), A ₁	2037 (m) ^[48] 2128 (vw) ^[48]	2038 (31), ν_{as} (CO), T ₂ 2105 (6), ν_s (CO), A ₁
avg. <i>d</i> (Ni-CO/Ni-NO) [Å]	1.847(9)	1.872	1.931(5)	1.975	1.827(3) ^[47]	1.842
avg. <i>d</i> (C-O/N-O) [Å]	1.124(6)	1.191	1.110(4)	1.119	1.138(1) ^[47]	1.135
avg. α (Ni-C-O/Ni-N-O) ^[c]	177.3(3)	179.4	177.8(5)	176.3	179.57(15) ^[47]	180
$\delta^{14}\text{N}$ NMR [ppm]	4.9	12.6	–	–	–	–
QTAIM charges <i>q</i> (Ni), <i>q</i> (CO), <i>q</i> (NO) [e]	–	0.72, 0.06, 0.10	–	0.77, 0.06, –	–	0.52, –0.13, –

[a] IR and Raman spectra were calculated at the BP86(D3BJ)/def2-TZVPP level of theory without scaling factor. All other calculated values in this table were determined using B3LYP(D3BJ)/def2-TZVPP. [b] Due to the low quality of the obtained Raman spectrum of **2**, only the frequencies of the carbonyl stretching modes without intensities are reported.

covalency of the M-NO back bonds, small changes in the charge distribution are sufficient to either assign both degenerate π -MOs to the metal, resulting in a formal NO⁺ ligand, or to allocate all four electrons to the ligand, resulting in a formal NO³⁻.^[41] Furthermore, complex **1** could be described as Ni^{II} (*S* = 1) antiferromagnetically coupled to a NO⁻ (*S* = 1).^[43] Due to the rather formal assignment, we decided to omit these expensive calculations, and thus we make no statement about the formal oxidation states in [Ni(CO)₃(NO)]⁺ and only refer to the NO stretching frequency at 1953 cm⁻¹ (compared to $\tilde{\nu}$ (NO⁺) = 2376 cm⁻¹, $\tilde{\nu}$ (NO⁰) = 1904 cm⁻¹, $\tilde{\nu}$ (NO⁻) = 1363 cm⁻¹)^[44] and the QTAIM charges (Table 2). The results indicate that the positive charge is mainly located on the metal atom.

Compared to the T_d symmetric Ni(CO)₄, the d⁹ complex [Ni(CO)₄]⁺ exhibits Jahn–Teller distortion and DFT calculations support a D_{2d} symmetric ground state. In the IR spectrum of crystalline **2** (Figure 1 b, Table 2) one CO stretch is visible at 2170 cm⁻¹. Also [Ni(CO)₄]⁺ in the gas phase (2179 cm⁻¹)^[44] and in solid neon matrix (2176.2 cm⁻¹)^[16] only revealed one band, blue-shifted relative to neutral gaseous Ni(CO)₄ at 2057 cm⁻¹ (T₂).^[46] The expected splitting of the IR-active T₂ CO stretching mode in neutral Ni(CO)₄ appears to be small in [Ni(CO)₄]⁺, which is supported by DFT calculations (2139 cm⁻¹ (B₂), 2137 cm⁻¹ (E), @BP86(D3BJ)/def2-TZVPP). The blue-shift results from the reduced π -back bonding in [Ni(CO)₄]⁺, which is also responsible for the elongated average Ni–C bond length (1.931(5) Å) and reduced average C–O distance (1.110(4) Å) in the crystal structure of **2**, compared to 1.827(3) Å^[47] and 1.138(1) Å^[47] in crystalline Ni(CO)₄ (see Table 2 for comparison). Two crystallographically independent [Ni(CO)₄]⁺ cations are present in the crystal structure of **2**. One of them shows an almost undistorted D_{2d} symmetry, just like the cation in **2-4FB**, whereas the other cation in **2** displays a slightly stronger distortion from the gas phase structure (Supporting Informa-

tion, Table S6).^[54] The X-band cw-EPR spectrum of solid microcrystalline **2** at 100 K includes an anisotropic signal with two principle *g*-values, which agree with DFT calculations of the 17 VE complex [Ni(CO)₄]⁺. The calculated spin density of [Ni(CO)₄]⁺ is mainly located on the metal atom (Figure 1 c).

With Evans NMR method^[49] a value of 2.35 μ_B (1.88 μ_B without diamagnetic correction) was obtained for the effective magnetic moment of **2** in 4FB, which roughly corresponds to the doublet expectation value of 1.73 μ_B (Supporting Information, Section 8). The cyclic voltammogram of **2** in 4FB (Figure 1 d) reveals a reversible redox process at 1.21 V against Fc^{+/0}/Fc. This agrees well with the calculated potential of the couple [Ni(CO)₄]^{+/0} in 4FB of 1.18 V against Fc^{+/0}/Fc (see the Supporting Information, Section 11 for details). This Ni^{+/0} potential is remarkably high compared to other Ni^{+/0} couples (for example, [Ni(bis(5H-dibenzo[a,d]cyclohepten-5-yl)amine)(PPh₃)]₂^{+/0} (–1.28 V),^[50] [Ni(P^{Ph}₂N^{Ph}-Tol)₂]₂^{+/0} (–1.08 V),^[51] [Ni(PPh₃)₃]^{+/0} (–1.06 V)^[52] and [Ni(cod)₂]^{+/0} (–0.68 V)^[52]). The π -back bonding and electron-withdrawing ability of CO compared to the other ligands with mostly σ -donating character might cause this high potential value, explaining why a strong oxidant like Ag^{+/0}/0.5I₂ is necessary for the clean synthesis of **2**.

The herein reported compounds **1** and **2** are novel textbook entries. Furthermore, they can be prepared in organic solvent in up to 1 g batches and are stable at room temperature. Preliminary work suggests that they can be used as starting material to expand the coordination chemistry of ionic nickel compounds in the rare oxidation state of +1.^[52,53]

Acknowledgements

The authors would like to thank Dr. H. Scherer and F. Bitgü for NMR measurements, Dr. T. Ludwig for pXRD measurement and Dr. D. Kratzert for help with scXRD measure-

ments. This work was funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation)—Project numbers 350173756; 417643975. The use of the SEM-EDX set up, acquired through the BMBF project EDELKAT (FKZ 03X5524), is gratefully acknowledged. We would like to thank Anita Becherer for support in obtaining SEM-EDX measurements. The authors acknowledge support by the state of Baden-Württemberg through bwHPC and the German Research Foundation (DFG) through grant no INST 40/467-1 and 575-1 FUGG (JUSTUS1 and 2 cluster). Open access funding enabled and organized by Projekt DEAL.

Conflict of interest

The authors declare no conflict of interest.

Keywords: carbonyl ligands · nickel · transition metals · weakly coordinating anions

- [1] L. Mond, C. Langer, F. Quincke, *J. Chem. Soc. Trans.* **1890**, 57, 749.
- [2] a) E. L. Muetterties, J. Stein, *Chem. Rev.* **1979**, 79, 479; b) A. Y. Khodakov, W. Chu, P. Fongarland, *Chem. Rev.* **2007**, 107, 1692.
- [3] a) H. Nakako, Y. Misumi, T. Masuda, L. Bencze, G. Szalai, *Polym. J.* **1998**, 30, 577; b) M. Ishio, T. Terashima, M. Ouchi, M. Sawamoto, *Polym. J.* **2010**, 42, 17.
- [4] a) R. Motterlini, L. E. Otterbein, *Nat. Rev. Drug Discovery* **2010**, 9, 728; b) C. C. Romão, W. A. Blättler, J. D. Seixas, G. J. L. Bernardes, *Chem. Soc. Rev.* **2012**, 41, 3571.
- [5] Q. Xu, *Coord. Chem. Rev.* **2002**, 231, 83.
- [6] a) P. J. Dyson, *Coord. Chem. Rev.* **2004**, 248, 2443; b) P. Braunstein, F. Naud, *Angew. Chem. Int. Ed.* **2001**, 40, 680; *Angew. Chem.* **2001**, 113, 702.
- [7] J. E. Ellis, *Organometallics* **2003**, 22, 3322.
- [8] C. Lorenz, M. Kaas, N. Korber, *Z. Anorg. Allg. Chem.* **2018**, 644, 1678.
- [9] H. Willner, F. Aubke, *Angew. Chem. Int. Ed. Engl.* **1997**, 36, 2402; *Angew. Chem.* **1997**, 109, 2506.
- [10] G. Bistoni, S. Rampino, N. Scafuri, G. Ciancaleoni, D. Zuccaccia, L. Belpassi, F. Tarantelli, *Chem. Sci.* **2016**, 7, 1174.
- [11] A. J. Lupinetti, G. Frenking, S. H. Strauss, *Angew. Chem. Int. Ed.* **1998**, 37, 2113; *Angew. Chem.* **1998**, 110, 2229.
- [12] a) G. Frenking, *J. Organomet. Chem.* **2001**, 635, 9; b) G. Frenking, C. Loschen, A. Krapp, S. Fau, S. H. Strauss, *J. Comput. Chem.* **2007**, 28, 117; c) J. Chatt, L. A. Duncanson, *J. Chem. Soc.* **1953**, 2939.
- [13] H. Willner, F. Aubke, *Organometallics* **2003**, 22, 3612.
- [14] C. Chi, J. Cui, X. Xing, G. Wang, Z.-P. Liu, M. Zhou, *Chem. Phys. Lett.* **2012**, 542, 33.
- [15] a) J. Herman, J. D. Foutch, G. E. Davico, *J. Phys. Chem. A* **2007**, 111, 2461; b) F. A. Khan, D. L. Steele, P. B. Armentrout, *J. Phys. Chem.* **1995**, 99, 7819; c) J. Cui, G. Wang, X. Zhou, C. Chi, Z. H. Li, Z. Liu, M. Zhou, *Phys. Chem. Chem. Phys.* **2013**, 15, 10224; d) D. A. Fredeen, D. H. Russell, *J. Am. Chem. Soc.* **1986**, 108, 1860; e) Š. Vajda, S. Wolf, T. Leisner, U. Busolt, L. H. Wöste, D. J. Wales, *J. Chem. Phys.* **1997**, 107, 3492.
- [16] B. Liang, M. Zhou, L. Andrews, *J. Phys. Chem. A* **2000**, 104, 3905.
- [17] J. R. Morton, K. F. Preston, *Inorg. Chem.* **1985**, 24, 3317.
- [18] a) M. K. Assefa, J. L. Devera, A. D. Brathwaite, J. D. Mosley, M. A. Duncan, *Chem. Phys. Lett.* **2015**, 640, 175; b) K. Mogi, Y. Sakai, T. Sonoda, Q. Xu, Y. Souma, *J. Phys. Chem. A* **2003**, 107, 3812; c) L. A. Barnes, M. Rosi, C. W. Bauschlicher, *J. Chem. Phys.* **1990**, 93, 609; d) K. Mogi, Y. Sakai, T. Sonoda, Q. Xu, Y. Souma, *J. Mol. Struct. THEOCHEM* **2001**, 537, 125.
- [19] E. Bernhardt, H. Willner, A. Kornath, J. Breidung, M. Bühl, V. Jonas, W. Thiel, *J. Phys. Chem. A* **2003**, 107, 859.
- [20] J. Bohnenberger, M. Schmitt, W. Feuerstein, I. Krummenacher, B. Butschke, J. Czajka, P. J. Malinowski, F. Breher, I. Krossing, *Chem. Sci.* **2020**, 11, 3592.
- [21] a) I. Krossing, I. Raabe, *Angew. Chem. Int. Ed.* **2004**, 43, 2066; *Angew. Chem.* **2004**, 116, 2116; b) T. A. Engesser, M. R. Lichtenthaler, M. Schleep, I. Krossing, *Chem. Soc. Rev.* **2016**, 45, 789; c) I. M. Riddlestone, A. Kraft, J. Schaefer, I. Krossing, *Angew. Chem. Int. Ed.* **2018**, 57, 13982; *Angew. Chem.* **2018**, 130, 14178.
- [22] H. Willner, F. Aubke, *Chem. Eur. J.* **2003**, 9, 1668.
- [23] J. Bohnenberger, W. Feuerstein, D. Himmel, M. Daub, F. Breher, I. Krossing, *Nat. Commun.* **2019**, 10, 624.
- [24] J. Geier, H. Willner, C. W. Lehmann, F. Aubke, *Inorg. Chem.* **2007**, 46, 7210.
- [25] J. Schaefer, A. Kraft, S. Reininger, G. Santiso-Quinones, D. Himmel, N. Trapp, U. Gellrich, B. Breit, I. Krossing, *Chem. Eur. J.* **2013**, 19, 12468.
- [26] W. Unkrig, M. Schmitt, D. Kratzert, D. Himmel, I. Krossing, *Nat. Chem.* **2020**, 12, 647.
- [27] E. Bernhardt, C. Bach, B. Bley, R. Wartchow, U. Westphal, I. H. T. Sham, B. von Ahsen, C. Wang, H. Willner, R. C. Thompson et al., *Inorg. Chem.* **2005**, 44, 4189.
- [28] 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.
- [29] S. C. Meier, A. Holz, A. Schmidt, D. Kratzert, D. Himmel, I. Krossing, *Chem. Eur. J.* **2017**, 23, 14658.
- [30] a) J. Bohnenberger, D. Kratzert, S. M. N. V. T. Gorantla, S. Pan, G. Frenking, I. Krossing, *Chem. Eur. J.* **2020**, 26, 17203; b) P. J. Malinowski, I. Krossing, *Angew. Chem. Int. Ed.* **2014**, 53, 13460; *Angew. Chem.* **2014**, 126, 13678.
- [31] J. Bohnenberger, I. Krossing, *Angew. Chem. Int. Ed.* **2020**, 59, 5581; *Angew. Chem.* **2020**, 132, 5629.
- [32] P. J. Malinowski, D. Himmel, I. Krossing, *Angew. Chem. Int. Ed.* **2016**, 55, 9259; *Angew. Chem.* **2016**, 128, 9405.
- [33] P. J. Malinowski, D. Himmel, I. Krossing, *Angew. Chem. Int. Ed.* **2016**, 55, 9262; *Angew. Chem.* **2016**, 128, 9408.
- [34] Under these conditions, neutral Ni(CO)₄ may be produced in situ, which is subsequently oxidized. Yet, although the commercial nickel powder was activated in a stream of hydrogen (10% in argon, 400 °C, 4 h) prior to use, no formation of a liquid phase could be observed after the nickel powder was stirred in 3 bar CO atmosphere in a closed reaction vessel at 75 °C for 20 h. Thus, presumably, the oxidation of elemental nickel would be the first step towards the formation of [Ni(CO)₄]⁺.
- [35] a) S. Dapprich, U. Pidun, A. W. Ehlers, G. Frenking, *Chem. Phys. Lett.* **1995**, 242, 521; b) M. Mitoraj, A. Michalak, *Organometallics* **2007**, 26, 6576.
- [36] A. W. Ehlers, S. Dapprich, S. F. Vyboishchikov, G. Frenking, *Organometallics* **1996**, 15, 105.
- [37] R. Kalescky, E. Kraka, D. Cremer, *Inorg. Chem.* **2014**, 53, 478.
- [38] In the mass spectrometer, also the 19 VE cation [Ni(CO)₅]⁺ was detected with even higher intensity than [Ni(CO)₄]⁺.^[14] Yet, the fifth CO from [Ni(CO)₅]⁺ is only weakly bound with an electronic energy of 36.4 kJ mol⁻¹ (@DLPNO-CCSD(T)/aug-cc-pVQZ//B3LYP(D3BJ)/def2-TZVPP, without ZPE). When including thermal and entropic contributions at RT the Gibbs energy for the dissociation of one CO is -5.6 kJ mol⁻¹ (Supporting Information, Section 11), which complies with the fact that we only isolated [Ni(CO)₄]⁺.
- [39] J. Bohnenberger, B. Derstine, M. Daub, I. Krossing, *Angew. Chem. Int. Ed.* **2019**, 58, 9586; *Angew. Chem.* **2019**, 131, 9687.
- [40] J. H. Enemark, R. D. Feltham, *Coord. Chem. Rev.* **1974**, 13, 339.

- [41] T. Ampßler, G. Monsch, J. Popp, T. Riggenmann, P. Salvador, D. Schröder, P. Klüfers, *Angew. Chem. Int. Ed.* **2020**, *59*, 12381; *Angew. Chem.* **2020**, *132*, 12480.
- [42] a) E. Ramos-Cordoba, V. Postils, P. Salvador, *J. Chem. Theory Comput.* **2015**, *11*, 1501; b) V. Postils, C. Delgado-Alonso, J. M. Luis, P. Salvador, *Angew. Chem. Int. Ed.* **2018**, *57*, 10525; *Angew. Chem.* **2018**, *130*, 10685.
- [43] N. C. Tomson, M. R. Crimmin, T. Petrenko, L. E. Rosebrugh, S. Sproules, W. C. Boyd, R. G. Bergman, S. DeBeer, F. D. Toste, K. Wieghardt, *J. Am. Chem. Soc.* **2011**, *133*, 18785.
- [44] K. P. Huber, G. Herzberg, *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules*, Springer, Boston, **1979**.
- [45] F. Eckert, A. Klamt, *AIChE J.* **2002**, *48*, 369.
- [46] L. H. Jones, *J. Chem. Phys.* **1958**, *28*, 1215.
- [47] L. J. Farrugia, C. Evans, *J. Phys. Chem. A* **2005**, *109*, 8834.
- [48] H. Stammreich, K. Kawai, O. Sala, P. Krumholz, *J. Chem. Phys.* **1961**, *35*, 2168.
- [49] a) D. F. Evans, *J. Chem. Soc.* **1959**, 2003; b) S. K. Sur, *J. Magn. Reson.* **1989**, *82*, 169.
- [50] M. Vogt, B. de Bruin, H. Berke, M. Trincado, H. Grützmacher, *Chem. Sci.* **2011**, *2*, 723.
- [51] V. V. Khrizanforova, V. I. Morozov, A. G. Strel'nik, Y. S. Spiridonova, M. N. Khrizanforov, T. I. Burganov, S. A. Katsyuba, S. K. Latypov, M. K. Kadirov, A. A. Karasik, et al., *Electrochim. Acta* **2017**, *225*, 467.
- [52] M. M. Schwab, D. Himmel, S. Kacprzak, V. Radtke, D. Kratzert, P. Weis, M. Wernet, A. Peter, Z. Yassine, D. Schmitz et al., *Chem. Eur. J.* **2018**, *24*, 918.
- [53] 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; *Angew. Chem.* **2015**, *127*, 14919; b) M. M. Schwab, D. Himmel, S. Kacprzak, Z. Yassine, D. Kratzert, C. Felbek, S. Weber, I. Krossing, *Eur. J. Inorg. Chem.* **2019**, 3309.
- [54] Deposition Numbers 2053747 (for **1**), 2053714 (for **2**), and 2053746 (for **2-4FB**) 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 www.ccdc.cam.ac.uk/structures.

Manuscript received: February 12, 2021

Revised manuscript received: March 15, 2021

Accepted manuscript online: March 18, 2021

Version of record online: May 2, 2021