

### Preliminary communication

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## A THERMALLY STABLE NICKEL(II) METALLOFORMATE AND ITS PLATINUM(II) ANALOGUE

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(Received October 14th, 1983)

### Summary

The terdentate monoanionic ligand  $o,o'$ -(Me<sub>2</sub>NCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (N—C—N) has been used to synthesize the air-stable metalloformate complexes [M(N—C—N)O<sub>2</sub>CH] (M = Ni, **1b**; Pt, **2b**). The platinum complex readily undergoes elimination of CO<sub>2</sub>. An X-ray analysis of **1b** shows an O-bonded formate ligand orientated perpendicular to the Ni coordination plane.

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The metal-bound formate (M—O<sub>2</sub>CH) and hydroxycarbonyl (M—CO<sub>2</sub>H) groupings are of importance owing to their postulated intermediacy in many metal catalysed processes [1]. Comparatively few organometallic complexes containing these functionalities have been well characterized since facile elimination of CO<sub>2</sub> often occurs with consequent formation of metal hydride species [2].

Using the terdentate anionic ligand  $o,o'$ -(Me<sub>2</sub>NCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (N—C—N) we have now isolated in good yield the solid air-stable organometallic complexes [M(N—C—N)O<sub>2</sub>CH] (M = Ni, **1b**; Pt, **2b**; eq. 1) which show a remarkable difference in stability in respect of subsequent carbon dioxide elimination. The white platinum complex, which undergoes slow thermal decomposition at 20°C, undergoes elimination of CO<sub>2</sub> in benzene at 50°C and, although [Pt(N—C—N)H] has not been identified, this reaction can be employed to synthesize [(N—C—N)Pt(μ-H)Pt(N—C—N)]<sup>+</sup> [3]. In contrast green yellow [Ni(N—C—N)O<sub>2</sub>CH], the first example of an organonickel formate species, can be recovered unchanged from boiling benzene and is sublimable at 130°C

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through an X-ray single-crystal structure determination (Fig. 1)\*. Greenish crystals of **1b**,  $C_{13}H_{20}NiN_2O_2$ , are monoclinic (space group  $P2_1/a$ , No. 14) with  $Z = 4$ ; unit cell dimensions  $a$  11.470(2),  $b$  11.007(2),  $c$  11.560(2) Å,  $\beta$  111.06(1)°,  $V$  1362.0(4) Å<sup>3</sup>,  $D_x$  1.439 g cm<sup>-3</sup>. The nickel centre has an approximately square-planar coordination geometry comprising two mutually *trans* N donor atoms, the C-bonded phenyl group of the N—C—N system and *trans* to this a planar O-bonded O<sub>2</sub>CH group. This formato ligand is orientated almost perpendicular to the coordination plane with a non-bonding Ni—O distance of 3.126(2) Å. In **1b** and two other crystallographically characterized metalloformates (*t*-[Pt{P(*c*-Hex)<sub>3</sub>]<sub>2</sub>H(O<sub>2</sub>CH)] [**2a**] and [CpFe(CO)<sub>2</sub>O<sub>2</sub>CH] [**2b**] the C—O distances are comparable and do not reflect the differing thermodynamic stabilities of these species.

Our studies of the CO<sub>2</sub> elimination reaction and of how it is influenced by the N—C—N ligand and the nature of the metal centre are now continuing with emphasis on **1b** [Ni<sup>II</sup>] as a precursor to unique Ni<sup>III</sup> formato derivatives.

**Acknowledgement.** This work was supported in part by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization of Pure Research (ZWO). The authors wish to thank Dr. A.J.M. Duisenberg for kindly collecting the X-ray data and Prof. K. Vrieze for helpful discussions.

## References

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\*3130 Reflections (CAD4F, Mo-K $\alpha$ ). Structure solved with standard Patterson and Fourier methods using 2593 independent reflections [ $I > 2.5\sigma(I)$ ] gives  $R_F = 0.026$ . Calculations were carried out using ILIAS, a DG-Eclipse S/230 adaptation and extension (by A.L. Spek) of the SHELX-76 package (by G. Sheldrick). The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by a full literature citation for this communication.