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Notes

Facile Preparation of $Ni_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_2$

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Summary: Reaction of $NiBr_2{\cdot}DME$ with $C_5Me_5MgCl{\cdot}THF$ at −30 °C followed by sequential treatment with CO and amalgamated zinc at 0 °C affords $Ni_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_2$ in reasonable yield. The compounds $[Ni(\eta^5\text{-}C_5Me_5)(CO)]^-M^+$ (M = Li, Na, PPN) have been synthesized and trapped with Ph_3SnCl, forming $Ni(\eta^5\text{-}C_5Me_5)(CO)(SnPh_3)$.

We have described synthetic routes to both $Pt_2(\eta^5\text{-}C_5Me_5)_2(CO)_2$ (**1**) and $Pd_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_2$ (**2**).[1] The nickel analogue $Ni_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_2$ (**3**) was first described by Mise and Yamazaki from direct treatment of $Ni(CO)_4$ and $C_5Me_5^-Li^+$.[2] Dahl et al. found this method failed to work unless the resultant mixture was oxidized with CuCl, purification being effected by column chromatography on alumina.[3] Although $Ni(CO)_4$ itself is inexpensive, the costs of handling it under increasingly stringent safety requirements are prohibitive. Since we required relatively large amounts of $Ni_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_2$, we sought an alternative route which avoided the use of $Ni(CO)_4$ and the need for preparative chromatography.

Kölle has reported the synthesis of $Ni_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}Br)_2$ (**4**) from $NiBr_2{\cdot}DME$ and C_5Me_5Li.[4] Although in our hands this reaction did not give reproducible results,[5] we found that reaction of $NiBr_2{\cdot}DME$ with a solution of the Grignard reagent $C_5Me_5MgCl{\cdot}THF$ in THF for 24 h at −30 °C reproducibly gave **4**. Subsequent treatment with CO caused the brown solution to darken due to the formation of $Ni(\eta^5\text{-}C_5Me_5)(CO)Br$.[6] Reduction of this solution with amalgamated zinc at 0 °C resulted in a further rapid color change to red. Removing all volatiles in vacuo, extracting into hexane, and cooling to −80 °C afforded $Ni_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_2$ (**3**) as red platelets in 57% yield.[7] The spectroscopic data for this material agree well with literature values.[2]

$Ni_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_2$ may also be prepared by treatment of $NiBr_2{\cdot}DME$ with 2 equiv of $C_5Me_5MgCl{\cdot}THF$ at −30 °C for 24 h followed by treatment with CO. There is no evidence for decamethylnickelocene being produced at this temperature,[8] and it is likely that $Ni(\eta^5\text{-}C_5Me_5)(CO)Br$ is formed and then reduced by the second equivalent of Grignard reagent in a manner analogous to that found in the preparation of $Pt_2(\eta^5\text{-}C_5Me_5)_2(CO)_2$.[1] Because of the potential problems of separation of the organic byproduct from complex **3**, we have not pursued this synthetic route. The methods outlined above failed to yield $Ni_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CO)_2$, presumably due to the instability of $Ni_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}Br)_2$.[9]

Dahl has reported[3] that the product obtained from the treatment of $Ni(CO)_4$ with $C_5Me_5^-Li^+$ is the anion $[Ni(\eta^5\text{-}C_5Me_5)(CO)]^-Li^+$. We were concerned that the value of ν(CO) reported for this anion, 1975 cm^{-1}, is remarkably high for an electron-rich species containing only one electron-withdrawing carbonyl group, even if contact ion pairing is taken into account. We have found that reduction of $Ni_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_2$ with 2 equiv of sodium or lithium naphthalenide readily affords the species $[Ni(\eta^5\text{-}C_5Me_5)(CO)]^-M^+$ (M = Na, **5a**; M = Li, **5b**).[10] Quenching the reaction mixture with Ph_3SnCl yields the expected derivative $Ni(\eta^5\text{-}C_5Me_5)(CO)(SnPh_3)$ (**6**). The values of ν(CO) found for the anions in THF solution (**5a**, 1793 cm^{-1}; **5b**, 1770 cm^{-1}) are in a more reasonable region than the value reported by Dahl. Furthermore, on addition of PPN^+Cl^- to either **5a** or **5b** the respective absorption bands attributable to ν(CO) shifted to a common value of 1826 cm^{-1}. This indicates that ion pairing predominates in the alkali-metal salts.[11]

The anions **5** are very air-sensitive, and accurate infrared spectra can only be obtained under rigorous anaerobic conditions. In the absence of these precautions, we have observed broad absorption bands between 2000 and 1900 cm^{-1}. Furthermore, as air slowly diffuses through the Teflon gasket of the solution cell into pure solutions of $[Ni(\eta^5\text{-}C_5Me_5)(CO)]^-$, the neutral dimer $Ni_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_2$ can slowly be seen to reform from the edge of the cell inward (complete oxidation takes about 15–20 min in our solution cells). It is thus tempting to speculate that the

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(1) Boag, N. M. *Organometallics* **1988**, *7*, 1446–1449. Boag, N. M.; Boucher, D.; Davies, J. A.; Miller, R. W.; Pinkerton, A. A.; Syed, R. *Organometallics* **1988**, *7*, 791–792.

(2) Mise, T.; Yamazaki, H. *J. Organomet. Chem.* **1979**, *164*, 391–400.

(3) Maj, J. J.; Rae, A. D.; Dahl, L. F. *J. Am. Chem. Soc.* **1982**, *104*, 3054–3063.

(4) Kölle, U.; Fuss, B.; Khouzami, F.; Gersdorf, J. *J. Organomet. Chem.* **1985**, *290*, 77–83.

(5) The problems seem to arise from the poor solubility of C_5Me_5Li, especially when this compound is prepared by precipitation via mixing hexane solutions of C_5Me_5H and Bu^nLi.

(6) Jutzi, P.; Mix, A. *Chem. Ber.* **1990**, *123*, 1043–1045.

(7) The complex $Pd_2(\eta^5\text{-}C_5Ph_5)_2(\mu\text{-}CO)_2$ may be prepared similarly: Powell, J.; Dowling, N. I. *Organometallics* **1983**, *2*, 1742–1748.

(8) Werner, H.; Dernberger, T. *J. Organomet. Chem.* **1980**, *198*, 97–103.

(9) Poli, R. *Chem. Rev.* **1991**, *91*, 509–552.

(10) $[Ni(\eta^5\text{-}C_5H_5)(CO)]^-$ has been similarly prepared: Gompper, R.; Bartmann, E. *Liebigs Ann. Chem.* **1980**, 229–240. See also: Jolly, P. W.; Wilke, G. *Organometallic Chemistry of Nickel*; Academic Press: New York, 1974; Vol. 1. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 6, Chapter 37.7. $[Ni(\eta^5\text{-}C_5H_5)(CO)]^-$ may also be prepared by reduction of $Ni_2(\eta^5\text{-}C_5H_5)_2$ with Na/K alloy in THF, whereas Na/Hg reduction in methanol affords the Fischer–Palm molecule $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$: Brown, J. M.; Conneely, J. A.; Mertis, K. *J. Chem. Soc., Perkin Trans. 2* **1974**, 905–907. Fischer, E. O.; Palm, C. *Chem. Ber.* **1958**, *91*, 1725–1731. Ellis, J. R.; Flom, E. A. *J. Organomet. Chem.* **1975**, *99*, 263–268.

(11) Several weak absorptions are seen to high and low wavenumber of the primary absorption reported. These may be due to impurities or to a different type of anion–cation association. We have yet to undertake the experiments necessary to confirm the source of the absorption bands: Darensbourg, M. Y. *Prog. Inorg. Chem.* **1985**, *33*, 221–274.

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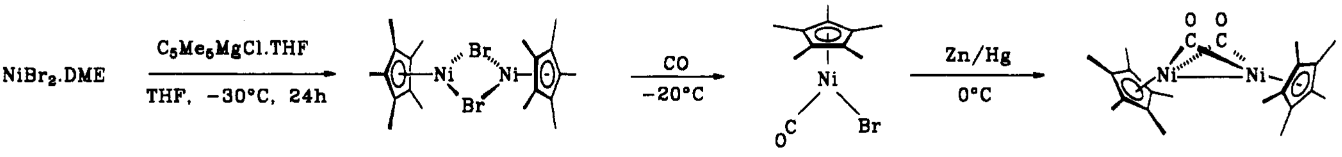
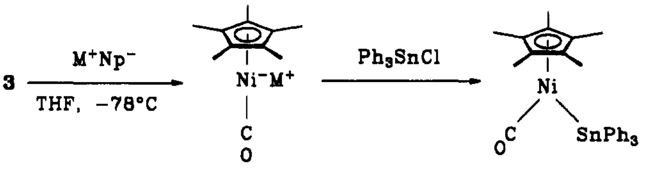
Scheme I



4

3

Scheme II



M = Na, **5a**

= Li, **5b**

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presence of small amounts of adventitious oxygen may lie at the root of the reported differences in the reaction of $Ni(CO)_4$ with $C_5Me_5^-Li^+$.[2,3]

Experimental Section

All manipulations were performed under an atmosphere of dinitrogen using standard Schlenk techniques. Solvents were freshly distilled from sodium/benzophenone (THF), sodium/potassium alloy (hexane), or phosphorus pentoxide (dichloromethane). The naphthalenide anion was prepared by stirring a THF solution of freshly sublimed naphthalene with the appropriate alkali metal overnight and the molarity of the solution determined by the difference in acid titrations of a sample quenched in water and one quenched initially in benzyl chloride. Infrared spectra were measured on a Perkin-Elmer 1710 Fourier transform spectrometer using CaF_2 solution cells fitted with Luer lock taps. NMR spectra were recorded on either a JEOL EX90 or a Bruker AC300 spectrometer. Elemental analyses were by Butterworth Laboratories, London.

$Ni_2(\eta^5\text{-}C_5Me_5)_2(CO)_2$ (3). A solution of C_5Me_5MgCl[12] (56 cm³ of a 0.32 M solution in THF) was added dropwise with stirring to a suspension of $NiBr_2{\cdot}DME$[4] (5 g, 17.93 mmol) in THF (50 cm³) at −30 °C. The solution was stirred for 24 h at the same temperature. Carbon monoxide was then bubbled through the solution of 10 min at −20 °C, the solution warmed to 0 °C, and amalgamated zinc (5 g) added. The solution was stirred for a further 30 min. The resulting claret solution was reduced to dryness in vacuo at 0 °C and the residue extracted into hexane and stored at −80 °C. Red platelike crystals were produced (2.32 g, 57%). Anal. Calcd for $C_{22}H_{30}O_2Ni_2$ (3): C, 59.52; H, 6.81. Found: C, 58.88; H, 7.05. IR (hexane): 1857, 1816 cm^{-1}. IR (THF): 1853, 1809 cm^{-1}. NMR (toluene-d_8): ^1H (δ 1.70 (s, Me); $^{13}C\{^1H\}$ δ 238.1 (CO), 101.3 (*C*Me), 9.2 (Me).

$Ni(\eta^5\text{-}C_5Me_5)(CO)(SnPh_3)$ (6). A THF solution of sodium naphthalenide (1.36 mmol) was added dropwise with stirring to a solution of $Ni_2(\eta^5\text{-}C_5Me_5)_2(CO)_2$ (302 mg, 0.68 mmol) in THF (20 cm³) maintained at −78 °C. The solution turned from red to brown. Stirring was continued for 20 min, and Ph_3SnCl was added (581 mg, 1.51 mmol). The solution was warmed to room temperature, and all volatiles were removed in vacuo. The residue was extracted into hexane and column chromatographed on grade IV silica gel at −30 °C. Naphthalene and a small amount of 3 were eluted with hexane. The product, $Ni(\eta^5\text{-}C_5Me_5)(CO)(SnPh_3)$, eluted as a reddish brown band with 10% CH_2Cl_2 in hexane. Crystallization from hexane at −80 °C afforded red-orange crystals of $Ni(\eta^5\text{-}C_5Me_5)(CO)(SnPh_3)$ (400 mg, 51%). Anal. Calcd for $C_{29}H_{30}OSnNi$ (6): C, 60.90; H, 5.29. Found: C, 61.05; H, 5.45. IR (hexane): 2001 cm^{-1}. NMR (benzene-d_6): ^1H δ 7.8–7.1 (m, 15 H, Ph), 1.62 (s, 15 H, Me, J(SnH) = 13.2 Hz); $^{13}C\{^1H\}$ δ 194.6 (CO), 143.8 (C_1, Ph, J(SnC) = 352 Hz), 137.7 ($C_{2,6}$, Ph, J(SnC) = 38 Hz), 128.5 ($C_{3,5}$, Ph, J(SnC) = 43 Hz), 128.4 (C_4, Ph), 102.0 (*C*Me), 10.4 (Me).

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Registry No. **3**, 69239-93-6; **4**, 101163-02-4; **5a**, 142781-14-4; **5b**, 81230-31-1; **6**, 142781-15-5; $NiBr_2{\cdot}DME$, 28923-39-9; C_5Me_5MgCl, 74430-27-6; Ph_3SnCl, 639-58-7; Ni, 7440-02-0.

OM9202175

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Neopentyl- or *tert*-Butylzinc Complexes with Diethylthio- or Diethylselenocarbamates: Precursors for Zinc Chalcogens

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Summary: A series of compounds with the general formula $RZnE_2CNEt_2$ ($R = Me_3CCH_2$, Me_3C; E = S, Se) have been synthesized, characterized, and used to grow thin films of ZnS or ZnSe by MOCVD. An X-ray crystal structure for $Me_3CCH_2ZnSe_2CNEt_2$ has been determined and shows the compound to be dimeric. The compound crystallizes in space group $P\bar{1}$, with a = 12.993 (3) Å, b = 12.631 (3) Å, c = 10.179 (2) Å, α = 94.96 (2)°, β = 109.75°, and γ = 106.48 (2)°.

Recently a substantial interest has developed in single-molecule precursors for the deposition of compound semiconductors by metalloorganic chemical vapor deposition (MOCVD). Suitable molecules for the deposition of III/V materials, such as InP and GaAs, have been developed by Bradley and Faktor[1] and Cowley and Jones.[2,3] A number of reports have also appeared concerning single-molecule precursors for the deposition of II/VI materials, and systems studied have included thio-

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[2] Cowley, A. H.; Benac, B. L.; Ekerdt, J. G.; Jones, R. A.; Kidd, K. B.; Lee, J. Y.; Miller, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 6248.

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