Inorganic Chemistry

Reactions of CO_2 and CS_2 with 1,2-Bis(di-*tert*-butylphosphino)ethane Complexes of Nickel(0) and Nickel(I)

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Reaction of CS_2 with $[(dtbpe)Ni]_2(\eta^2,\mu\text{-}C_6H_6)$ (**1**; dtbpe =1,2-bis(di-*tert*-butylphosphino)ethane) in toluene gives the carbon disulfide complex $(dtbpe)Ni(\eta^2\text{-}CS_2)$ (**2**), characterized by standard spectroscopic methods and X-ray crystallography. Reaction of CS_2 with the Ni(I) complex $(dtbpe)Ni(OSO_2CF_3)$ gives the diamagnetic, trimetallic cluster $[\{(dtbpe)Ni(\kappa^1,\eta^2\text{-}CS_2)\}_2(dtbpe)Ni][SO_3CF_3]_2$ (**3-OTf**). The solid-state structure of **3-OTf** reveals that the two CS_2 ligands bind η^2 to two (dtbpe)Ni centers and κ^1 to the third, unique (dtbpe)Ni in the complex dication, and NMR spectroscopic data indicate that this structure is maintained in solution. Oxidation of **2** by ferrocenium hexafluorophosphate affords the identical trimetallic complex dication as the PF_6^- salt, $[\{(dtbpe)Ni(\kappa^1,\eta^2\text{-}CS_2)\}_2(dtbpe)Ni][PF_6]_2$ (**3-PF$_6$**). These results are consistent with the intermediacy of a $Ni(I)-CS_2$ complex, $[(dtbpe)Ni(CS_2)^+]$, that is unstable with respect to disproportionation. Reaction of **1** with one equivalent of CO_2 provides the carbon dioxide adduct $(dtbpe)Ni(\eta^2\text{-}CO_2)$ (**4**), that was also crystallographically characterized. Thermolysis of **4** in benzene solution at 80 °C results in reduction of the CO_2 ligand to CO, trapped as $(dtbpe)Ni(CO)_2$, and partial oxidation of a dtbpe ligand to give $O=P(\textit{tert}\text{-Bu})_2CH_2CH_2P(\textit{tert}\text{-Bu})_2$.

Introduction

Research directed toward developing new catalysts for converting CO_2 into fuels, chemicals, and polymeric materials has seen recent dramatic growth.[1-3] Since CO_2 is the terminal oxidation product of organic matter, it is the ultimate renewable C_1 feedstock, and its chemical utilization represents recycling of carbon into useful materials at the most basic level. It is also both abundant and cheap, and, because atmospheric CO_2 is a deleterious greenhouse gas, it has an effective negative cost as a chemical feedstock.[4]

The first structurally characterized CO_2 adduct of a transition metal was Aresta's $(PCy_3)_2Ni(\eta^2\text{-}CO_2)$.[5] Since its report, several examples of late transition-metal carbon dioxide coordination compounds have appeared featuring various binding modes.[3b,5] Carbon dioxide complexes of nickel are particularly relevant because they are implicated in biological systems that reduce CO_2, such as the C-cluster of Ni carbon monoxide dehydrogenase, in which nickel shuttles through several oxidation states.[6] We have been interested in transformations and redox processes involving $(dtbpe)NiL_x$ complexes (dtbpe = 1,2-bis(di-*tert*-butylphosphino)ethane) in the 0, +1, +2, and +3 oxidation states[7] and sought to investigate the binding of nickel with CO_2 and its sulfur

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(1) (a) Arakawa, H.; Aresta, M.; Armor, J. N.; Barteau, M. A.; Beckman, E. J.; Bell, A. T.; Bercaw, J. E.; Creutz, C.; Dinjus, E.; Dixon, D. A.; Domen, K.; DuBois, D. L.; Eckert, J.; Fujita, E.; Gibson, D. H.; Goddard, W. A.; Goodman, D. W.; Keller, J.; Kubas, G. J.; Kung, H. H.; Lyons, J. E.; Manzer, L. E.; Marks, T. J.; Morokuma, K.; Nicholas, K. M.; Periana, R.; Que, L.; Rostrup-Nielson, J.; Sachtler, W. M. H.; Schmidt, L. D.; Sen, A.; Somorjai, G.; Stair, P. C.; Stults, B. R.; Tumas, W. *Chem. Rev.* **2001**, *101*, 953–996. (b) Aresta, M.; Dibenedetto, A. *Dalton Trans.* **2007**, 2975–2992. (c) Benson, E. E.; Kubiak, C. P.; Sathrum, A. J.; Smieja, J. M. *Chem. Soc. Rev.* **2009**, *38*, 89–99.

(2) (a) Morgenstern, D. A.; Wittrig, R. E.; Fanwick, P. E.; Kubiak, C. P. *J. Am. Chem. Soc.* **1993**, *115*, 6470–6471. (b) DeLaet, D. L.; Fanwick, P. E.; Kubiak, C. P. *Chem. Commun.* **1987**, 1412–1413. (c) Simon-Manso, E.; Valderrama, M.; Arancibia, V.; Simon-Manso, Y.; Boys, D. *Inorg. Chem.* **2000**, *39*, 1650–1654. (d) Simon-Manso, E.; Kubiak, C. P. *Organometallics* **2005**, *24*, 96–102.

(3) (a) Laitar, D. S.; Muller, P.; Sadighi, J. P. *J. Am. Chem. Soc.* **2005**, *127*, 17196–17197. (b) Lee, C. H.; Laitar, D. S.; Mueller, P.; Sadighi, J. P. *J. Am. Chem. Soc.* **2007**, *129*, 13802–13803. (c) Lu, C. C.; Sauoma, C. T.; Day, M. W.; Peters, J. C. *J. Am. Chem. Soc.* **2007**, *129*, 4–5. (d) Tekavec, T. N.; Arif, A. M.; Louie, J. *Tetrahedron* **2004**, *60*, 7431–7437. (e) Louie, J.; Gibby, J. E.; Farnworth, M. V.; Tekavec, T. N. *J. Am. Chem. Soc.* **2002**, *124*, 15188–15189.

(4) Whitesides, G. M.; Crabtree, G. W. *Science* **2007**, *315*, 796–798.

(5) (a) Aresta, M.; Nobile, C. F.; Albano, V. G.; Forni, E.; Manassero, M. *J. Chem. Soc. Chem. Commun.* **1975**, 636–637. (b) Aresta, M.; Nobile, C. F. *J. Chem. Soc., Dalton Trans.* **1977**, 708–711. (c) Aresta, M.; Gobetto, R.; Quaranta, E.; Tommasi, I. *Inorg. Chem.* **1992**, *31*, 4286–4290.

(6) (a) Jeoung, J.-H.; Dobbek, H. *Science* **2007**, *318*, 1461–1464. (b) Lindahl, P. A. *Biochemistry* **2002**, *41*, 2097–2105. (c) Riordan, C. G. *J. Biol. Inorg. Chem.* **2004**, *9*, 542–549.

(7) (a) Mindiola, D. J.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2001**, *123*, 4623–4624. (b) Melenkivitz, R.; Mindiola, D. J.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2002**, *124*, 3846–3847. (c) Mindiola, D. J.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2002**, *124*, 9976–9977. (d) Mindiola, D. J.; Waterman, R.; Jenkins, D. M.; Hillhouse, G. L. *Inorg. Chim. Acta* **2003**, *345*, 299–308. (e) Kitiachvili, K. D.; Mindiola, D. J.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2004**, *126*, 10554–10555.

congener, CS_2, and to study their redox reactivity. Herein we describe the preparation of (dtbpe)Ni(0) CO_2 and CS_2 adducts and the results of their oxidation using the ferrocenium ion as an outer-sphere 1-e⁻ oxidant.

Experimental Section

General Considerations. Unless indicated otherwise, all operations were carried out in an MBraun LabMaster glovebox under an atmosphere of purified N_2 or by using high-vacuum and standard Schlenk techniques under Ar. Hexane, petroleum ether, and toluene were dried by passing the solvent through both activated alumina and Q-5 columns. All other solvents were dried and degassed by using standard high-vacuum and Schlenk techniques.[8] C_6D_6 and CD_2Cl_2 were purchased from Cambridge Isotope Laboratories, dried over CaH_2, and then degassed. Celite was dried by heating at 200 °C under vacuum for 12 h. Complexes [(dtbpe)Ni]$_2$(η^2-μ-C_6H_6) (**1**)[9] and (dtbpe)-Ni(OSO$_2$CF$_3$)[10] were prepared according to literature procedures. Infrared spectra (Fluorolube mull on CaF_2 plates or Nujol mull on KBr plates) were taken using a Nicolet Nexus 670 FT-IR. GC-MS data were obtained on a Varian Saturn 2200 instrument. Elemental analyses were obtained from Desert Analytics (Tucson, AZ). ^1H, ^{13}C, and ^{31}P NMR data were recorded on Bruker 500- and 400-MHz spectrometers. ^1H and ^{13}C NMR data are reported with reference to solvent resonances (for ^1H NMR: residual C_6D_5H in C_6D_6, 7.16 ppm; residual CHDCl$_2$ in CD_2Cl_2, 5.32 ppm. For ^{13}C NMR: C_6D_6, 128.0 ppm; CD_2Cl_2, 54.0 ppm). ^{31}P data are reported with respect to external 85% H_3PO_4 (0 ppm). X-ray diffraction data were collected on a Bruker platform goniometer equipped with a charged coupled device (CCD) detector (Smart Apex). The crystal structures were solved by direct methods using the SHELXTL (version 5.1) program library.[11]

Synthesis of (dtbpe)Ni(η^2-CS_2), 2. A dark-orange toluene solution of **1** (0.075 g, 0.09 mmol) was cooled to −35 °C. To the cold, stirred solution was added in a dropwise fashion an excess of CS_2 (0.1 mL, 1.66 mmol). The dark-orange color of the solution gradually lightened to a light orange as the solution was warmed to ambient temperature over a 1 h period. Removal of toluene under vacuum afforded a yellow-orange powder that was recrystallized from THF/hexanes at −35 °C to give light-orange crystals of **2** (0.072 g, 88%). Crystals suitable for X-ray diffraction studies were obtained by recrystallization from a concentrated toluene solution at −35 °C. For **2**: ^1H NMR (22 °C, 400 MHz, C_6D_6): δ 1.33 (m, CH_2CH_2, 2H), 1.28 (d, C(CH_3)$_3$, J_{HP} = 12.8 Hz, 18H), 1.17 (m, CH$_2$CH_2, 2H), 1.06 (d, C(CH_3)$_3$, J_{HP} = 12.2 Hz, 18H). $^{31}P\{^1H\}$ NMR (22 °C, 202.4 MHz, C_6D_6): AB quartet δ 80.72 (apparent J = 33 Hz), 80.23 (apparent J = 33 Hz). $^{13}C\{^1H\}$ NMR (22 °C, 125 MHz, C_6D_6): δ 264.20 (d, CS_2, J_{CP} = 50.3 Hz), 36.13 (dd, CH$_2$CH$_2$, J_{CP} = 14.0, 2.8 Hz), 34.20 (dd, CH$_2$CH$_2$, J_{CP} = 8.8, 2.0 Hz), 30.46 (d, C(CH$_3$)$_3$, J_{CP} = 4.7 Hz), 30.09 (d, C(CH$_3$)$_3$, J_{CP} = 5.0 Hz), 24.34 (t, C(CH$_3$)$_3$, J = 18.7 Hz), 20.43 (dd, C(CH$_3$)$_3$, J_{CP} = 14.02, 11.25 Hz). IR (Nujol, KBr): 1389 (s), 1368 (s), 1278 (w), 1179 (s), 1145 (vs), 1102 (m), 1088 (m), 1021 (s) 937 (w), 849 (m), 814 (s), 787 (s), 727 (w), 681 (m), 657 (m), 639 (vs), 606 (m), 580 (m), 495 (s), 453 (m), 427 (w) cm⁻¹. Anal. (%) calcd for $C_{19}H_{40}NiP_2S_2$: C, 50.34; H, 8.89. Found: C, 50.47; H, 8.87.

(8) Burger, B. J.; Bercaw, J. E. In *Experimental Organometallic Chemistry; ACS Symposium Series 357*; Wayda, A. L., Darensbourg, M. Y., Eds.; American Chemical Society; Washington, DC, 1987; pp 79−98.

(9) Bach, I.; Pörschke, K.; Goddard, R.; Kopiske, C.; Kruger, C.; Rufinska, A.; Seevogel, K. *Organometallics* **1996**, *15*, 4959–4966.

(10) Iluc, V. M.; Miller, A. J. M.; Hillhouse, G. L. *Chem. Commun.* **2005**, 5091–5093.

(11) All software and sources of scattering factors are contained in: Sheldrick, G. *SHELXTL*, version 5.1; Bruker Analytical X-ray Systems, Madison, WI, 1998.

Synthesis of [{(dtbpe)Ni(κ^1,η^2-CS_2)}$_2$(dtbpe)Ni][SO$_3$CF$_3$]$_2$, 3-OTf. A golden toluene solution of (dtbpe)Ni(OSO$_2$CF$_3$) (0.053 g, 0.10 mmol) was cooled to −35 °C, and an excess of CS_2 (0.06 mL, 1.0 mmol) was added dropwise, resulting in an immediate color change of the solution to dark red with concurrent formation of a dark-red precipitate. The solution was allowed to stir for 30 min, and then the solvent was removed under vacuum. Recrystallization from THF/hexanes yielded red crystals of **3-OTf** (0.032 g, 60% yield). For **3-OTf**: ^1H NMR (22 °C, 500 MHz, CD_2Cl_2): δ 1.53 (d, C(CH_3)$_3$, J_{HP} = 13.2 Hz, 18H), 1.33 (d, C(CH_3)$_3$, J_{HP} = 13.2 Hz, 18H), 1.27 (d, C(CH_3)$_3$, J_{HP} = 13.6 Hz, 18H). $^{31}P\{^1H\}$ NMR (22 °C, 202.4 MHz, CD_2Cl_2): δ 96.47 (d, P(C(CH$_3$)$_3$)$_2$, J_{PP} = 11.1 Hz), 92.61 (vt, P(C(CH$_3$)$_3$)$_2$, J_{PP} = 10.3 Hz), 85.06 (d, P(C(CH$_3$)$_3$)$_2$, J_{PP} = 10.1 Hz). $^{13}C\{^1H\}$ NMR (22 °C, 125 MHz, CD_2Cl_2): δ 274.15 (m, CS_2), 38.97 (d, CH$_2$CH$_2$, J_{CP} = 14.5 Hz), 36.21 (d, CH$_2$CH$_2$, J_{CP} = 17.4 Hz), 35.12 (d, CH$_2$CH$_2$, J_{CP} = 15.2 Hz), 30.79 (s, C(CH$_3$)$_3$), 30.30 (dd, C(CH$_3$)$_3$, J_{CP} = 17.4, 4.2 Hz), 25.35 (dd, C(CH$_3$)$_3$, J_{CP} = 21.6, 14.9 Hz), 23.85 (dd, C(CH$_3$)$_3$, J_{CP} = 17.5, 13.6 Hz), 21.58 (dd, C(CH$_3$)$_3$, J_{CP} = 19.6, 8.9 Hz).

Synthesis of [{(dtbpe)Ni(κ^1,η^2-CS_2)}$_2$(dtbpe)Ni][PF$_6$]$_2$, 3-PF$_6$. In a 20 mL scintillation vial, **2** (0.032 g, 0.071 mmol) was dissolved in a minimum of THF and cooled to −35 °C. To this was added a cold (−35 °C) THF suspension of [Cp$_2$Fe][PF$_6$] (0.015 g, 0.047 mmol). Upon addition, an immediate color change of the solution to a dark red was observed, and the mixture was allowed to stir for 30 min. The solvent was removed under vacuum, and the dark-red solid was triturated with hexanes to remove Cp$_2$Fe. Upon recrystallization of the remaining solid from THF/hexanes, red crystals of **3-PF$_6$** were obtained (0.035 g, 95%). For **3-PF$_6$**: ^1H, ^{31}P, and ^{13}C NMR spectra for **3-PF$_6$** were identical to those of **3-OTf** with the exception of an additional peak in the $^{31}P\{^1H\}$ spectrum at δ −145.7 (sept, PF_6). Anal. (%) calcd for $C_{56}H_{120}F_{12}Ni_3P_8S_4$: C, 42.74; H, 7.69. Found: C, 42.22; H, 7.47.

Synthesis of (dtbpe)Ni(η^2-CO_2), 4. A 25 mL Schlenk flask was charged with a 10 mL hexane solution of **1** (0.048 g, 0.06 mmol). The solution was cooled to −78 °C, and then carbon dioxide (0.13 mmol) was added via syringe. The solution was stirred for 30 min at −78 °C before being gradually warmed to ambient temperature. During this time, the color of the solution gradually lightened to give a cloudy yellow solution. Yellow crystals of **4** (0.044 g, 91%) were obtained upon removal of solvent and could be recrystallized from a concentrated toluene solution cooled to −35 °C. Crystals suitable for X-ray diffraction studies were obtained on recrystallization from a mixture of THF and hexane at −35 °C. For **4**: ^1H NMR (22 °C, 400 MHz, C_6D_6): δ 1.19 (d, C(CH_3)$_3$, J_{HP} = 13.0 Hz, 18H), 1.11 (m, CH_2CH_2, 4H), 1.08 (d, C(CH_3)$_3$, J_{HP} = 12.3 Hz, 18H). $^{31}P\{^1H\}$ NMR (22 °C, 162 MHz, C_6D_6): δ 96.6 (d, P(C(CH$_3$)$_3$)$_2$, J_{PP} = 71 Hz), 71.0 (d, P(C(CH$_3$)$_3$)$_2$, J_{PP} = 71 Hz). $^{13}C\{^1H\}$ NMR (22 °C, 125 MHz, C_6D_6): δ 164.28 (d, CO_2, J_{CP} = 53.3 Hz), 34.41 (dd, CH$_2$CH$_2$, J_{CP} = 17.9, 3.5 Hz), 33.82 (dd, CH$_2$CH$_2$, J_{CP} = 7.3, 1.9 Hz), 30.22 (t, C(CH$_3$)$_3$, J_{CP} = 6.0 Hz), 23.15 (t, C(CH$_3$)$_3$, J = 18.6 Hz), 19.84 (dd, C(CH$_3$)$_3$, J_{CP} = 14.6, 9.9 Hz). IR (Nujol, KBr): 1724 (s), 1180 (m), 1125 (s), 1070 (s), 1020 (m), 937 (w), 850 (w), 815 (m), 786 (m), 732 (s), 679 (s). 662 (s), 608 (m), 584 (w), 543 (vw), 507 (w), 493 (w), 478 (w), 454 (w), 426 (w) cm⁻¹. Anal. (%) calcd for $C_{19}H_{40}NiO_2P_2$: C, 54.18; H, 9.57. Found: C, 54.15; H, 10.08.
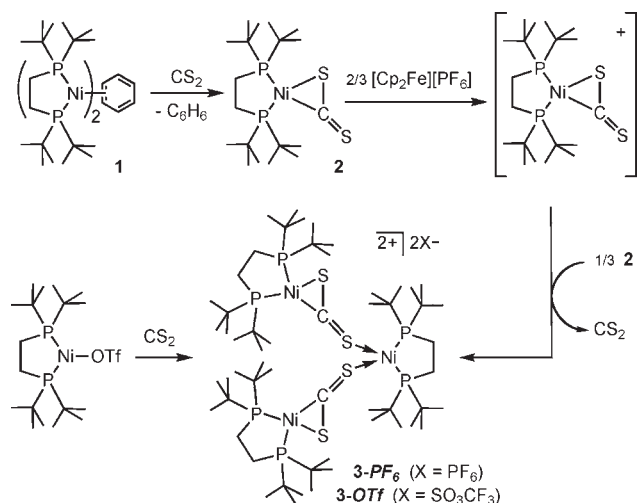
Synthesis of O=P-tert-Bu$_2$CH$_2$CH$_2$P-tert-Bu$_2$, 5. A 0.029 g-sample of **1** (0.064 mmol) was dissolved in 7 mL of pentane and placed in a 15 mL round-bottomed flask that was then sealed with a septum. The flask was cooled to −78 °C, and O_2 (0.8 mL, 1 atm, 0.033 mmol) was added via syringe under Ar. The resulting solution was warmed to ambient temperature and stirred for 30 min during which the solution's color gradually darkened to black. Filtration removed a black solid, and the resulting solution was dried under reduced pressure to yield **5** as a tan-gray solid (0.017 g, 76%). For **5**: ^1H NMR (22 °C,

Scheme 1. Reactions of CS_2 with Ni(0) and Ni(I) Bisphosphine Complexes

Figure 1. A perspective view of the structure of **2** with H atoms omitted for clarity and thermal ellipsoids drawn at 35% probability. The selected distances (Å) and angles (°) listed are the average of the two independent molecules in the unit cell with the average standard errors in brackets. Ni(1)−S(11) = 2.147[2], Ni(1)−C(1) = 1.922[5], C(1)−S(11) = 1.732[6], C(1)−S(12) = 1.583[6], S(11)−C(1)−S(12) = 137.7[4], C(1)−Ni(1)−S(11) = 50.0[2], C(1)−Ni(1)−P(12) = 108.9[2], S(11)−Ni(1)−P(11) = 108.87[7], and P(11)−Ni(1)−P(12) = 92.27[6].

400 MHz, C_6D_6): δ 1.98 (s, C_2H_4, 4 H), 1.12 (t, C(CH_3)$_3$, 36 H, J_{HP} = 11.8 Hz). $^{31}P\{^1H\}$ NMR (22 °C, 161 MHz, C_6D_6): δ 57.95 (d, O*P*(C(CH$_3$)$_3$)$_2$, J_{PP} = 42.8 Hz), 38.07 (d, *P*(C(CH$_3$)$_3$)$_2$, J_{PP} = 42.8 Hz). GC-MS (*m/z*) 335 (M$^+$).

Thermolysis of 4. A sample of **4** (0.010 g, 0.024 mmol) was dissolved in 0.6 mL of C_6D_6, placed in a J-Young NMR tube, and sealed under N_2. The sample was heated at 80 °C for 72 h, after which mono-oxidized phosphine **5** (40% yield based on **4**), (dtbpe)Ni(CO)$_2$ (20% yield; $^{31}P\{^1H\}$ NMR δ 94.8),[12] unreacted **4** (~20%) was obtained as indicated by ^{31}P NMR and by comparison to the spectra of authentic samples. A black precipitate was also noted.

X-ray Crystal Structures of 2, 3-OTf and 4. X-ray quality crystals were obtained by slow crystallization at −35 °C from concentrated toluene or THF solutions layered with hexanes, as described above. A suitable crystal was chosen and mounted on the diffractometer. All nonhydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated positions. The **3-OTf** was crystallized with 2.5 molecules of THF. For **3-OTf**, the asymmetric unit contains the complex dication, one triflate anion, 0.5 triflate anion on an inversion center disordered over two positions, a triflate anion, which alternates with a THF molecule (50% occupancy each), and two additional THF molecules. Overall each unit cell contains two complex dications, four triflate anions, and five molecules of THF.

Results and Discussion

Reaction of a cold, dark-orange toluene solution of [(dtbpe)-Ni]$_2$(η^2,u-C_6H_6) (**1**)[9] with an excess of carbon disulfide results in a gradual lightening in the color of the solution over a 1 h period to provide (dtbpe)Ni(η^2-CS_2) (**2**) as analytically pure orange crystals in 88% yield (Scheme 1). The ^1H NMR spectrum of **2** displays two sets of inequivalent *t*-butyl groups, and the $^{31}P\{^1H\}$ spectrum shows an AB quartet for the inequivalent phosphorus atoms in the η^2-Ni(CS_2) adduct.

Crystals of **2** suitable for X-ray diffraction were grown from a concentrated toluene solution at −35 °C. The molecular structure of one of two independent molecules in the unit cell of **2** is shown in Figure 1 (see also Table 1) and indicates a square-planar geometry at nickel. The uncoordinated C(1)−S(12) bond at 1.583(6) Å is typical for a C=S
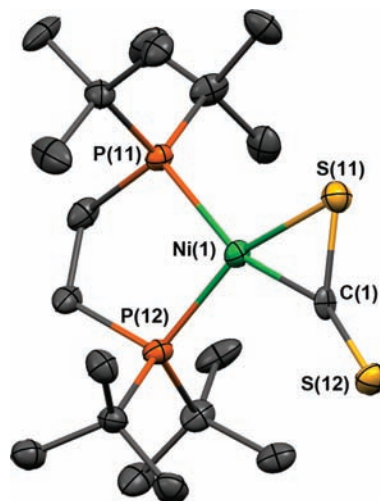
double bond, and the coordinated C(1)−S(11) bond length of 1.732(6) Å (average of the two independent molecules) indicates a large degree of backbonding from the nickel center into the π* orbital of the ligated C=S unit. The latter distance is significantly longer than the corresponding value of 1.63(1) Å found in [MeC(CH$_2$PPh$_2$)$_3$]Ni(η^2-CS_2).[13] Although other four-coordinate nickel CS_2 complexes of the type (PR$_2$CH$_2$CH$_2$PR$_2$)Ni(η^2-CS_2) (R = Cy, Ph) have been reported, they have not been crystallographically characterized.[14] The infrared spectrum of **2** shows stretches of 1145 and 639 cm^{-1} for $\nu_{C=S}$ and ν_{C-S}, respectively, which are similar to the values of 1150 and 630 cm^{-1} observed for [MeC(CH$_2$PPh$_2$)$_3$]Ni(η^2-CS_2).[13]

To probe whether we could access a Ni(I) analogue of **2**, we reacted a golden-colored toluene solution of the three-coordinate Ni(I) triflate complex (dtbpe)Ni(OSO$_2$CF$_3$)[10] with an excess of CS_2. Dropwise addition of CS_2 at −35 °C results in an immediate color change to give a dark-red solution from which the diamagnetic, trimetallic salt [{(dtbpe)Ni-(κ^1,η^2-CS_2)}$_2$(dtbpe)Ni][SO$_3$CF$_3$]$_2$ (**3-OTf**) was isolated in high yield (Scheme 1). Moreover, a similar dicationic complex is formed in the reaction of a cold THF solution of **2** with two-thirds of an equivalent of the outer-sphere oxidant [Cp$_2$Fe][PF$_6$]; from this dark-red reaction mixture, [{(dtbpe)-Ni(κ^1,η^2-CS_2)}$_2$(dtbpe)Ni][PF$_6$]$_2$ (**3-PF$_6$**) was isolated in 95% yield. In both reactions, it is likely that a Ni(I)−CS_2 intermediate [(dtbpe)Ni(CS_2)]$^+$ is initially formed, but it rapidly undergoes disproportionation to give the observed trimetallic cluster. Complexes **3-OTf** and **3-PF$_6$** were characterized by their ^1H and ^{31}P NMR spectra, elemental analysis, and X-ray crystallographic analysis of a THF-solvated form of **3-OTf**. The NMR data suggest static solution structures for **3-OTf** and **3-PF$_6$** in which the nickels do not exchange sites in the cluster.

(12) Pörschke, K.-R.; Pluta, C.; Proft, B.; Lutz, F.; Krüger, C. *Z. Naturforsch.* **1993**, *48B*, 608.

(13) Bianchini, C.; Masi, D.; Mealli, C. C.; Meli, A. *Inorg. Chem.* **1984**, *23*, 2838–2844.

(14) (a) Bennett, M. A.; Johnson, J. A.; Willis, A. C. *Organometallics* **1996**, *15*, 68–74. (b) Yamamoto, T.; Kohara, T.; Osakada, K.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2147–2153.

Table 1. Crystallographic Data for Structurally Characterized Compounds[a]

compound	2	3-OTf·2.5(THF)	4
empirical formula	$C_{19}H_{40}NiP_2S_2$	$C_{68}H_{140}F_6Ni_3O_{8.5}P_6S_6$	$C_{19}H_{40}NiO_2P_2$
formula weight	453.28	1762.11	421.16
space group	$P2_1$	$P2_1/c$	$P2_1/n$
a (Å)	8.038(2)	11.0008(10)	8.3476(14)
b (Å)	27.870(7)	49.920(4)	19.212(3)
c (Å)	10.955(3)	16.1470(14)	13.814(2)
β (°)	110.422(4)	100.975(2)	90.050(3)
V (Å^3)	2299.9(10)	8705.1(13)	2215.3(6)
Z	4	2	4
Θ range (lattice, °)	1.46−28.28	1.52−25.00	1.82−25.00
D_{calc} (Mg/m^3)	1.309	1.345	1.263
μ (mm^{-1})	1.165	0.957	1.029
$F(000)$	976	3760	912
crystal color	orange	red	yellow
crystal form	block	block	plate
crystal size (mm^3)	0.05 × 0.03 × 0.02	0.05 × 0.03 × 0.02	0.05 × 0.02 × 0.02
reflections collected	13 335	45 226	11 577
ind reflections (R$_{int}$[b])	10 088 (0.0583)	15 292(0.0931)	3884(0.0756)
h, k, l ranges	−18 8, −35 36, −14 13	−13 13, −59 39, −19 19	−9 9, −19 22, −16 16
data/restraints/param.	10088/1/451	15292/0/943	3884/3/229
GoF on F^{2c}	1.025	1.068	0.927
F. R ind. [$I > 2\,\sigma(I)$][d]	R_1 = 0.0700	R_1 = 0.0886	R_1 = 0.0340
	wR_2 = 0.1695	wR_2 = 0.1629	wR_2 = 0.0760
R indices (all data)[e]	R_1 = 0.0761	R_1 = 0.1437	R_1 = 0.0426
	wR_2 = 0.1734	wR_2 = 0.1775	wR_2 = 0.0781
largest diff. peak	1.411	0.862	0.546
and hole (eÅ^{-3})	−0.562	−0.635	−0.218

[a] Common features to all crystals: monoclinic ($\alpha = \gamma = 90°$), $T = 100$ K, and $\lambda = 0.71073$ Å. Refinement method: full-matrix least squares on F^2, and absorption correction: semi-empirical from psi scans. [b] $R_{int} = \sum |F_o^2 − <F_o^2>|/\sum |F_o^2|$. [c] Goodness-of-Fit = $S = [\sum[w(F_o^2 − F_c^2)^2]/(n − p)]^{1/2}$. [d] $R_1 = \sum ||F_o| − |F_c||/\sum |F_o|$ [e] $wR_2 = [\sum[w(F_o^2 − F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$ for: $w = q/\sigma^2(F_o^2) + (aP)^2 + bP$, n = number of independent reflections, p = number of parameters refined, and weighting scheme $w = q [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$ where: $P = (F_o^2 + 2 F_c^2)/3$, $a =$, $b =$, $q = 1$.

The crystal structure of **3-OTf** (see Figure 2 and Supporting Information) reveals two CS_2 molecules bound in the coordination sphere of three Ni centers. A κ^1,η^2-CS_2 bridging mode was postulated in Wilkinson's early report of [(PPh$_3$)-Ni(CS_2)]$_2$ and later crystallographically confirmed,[15] but this sort of trimetallic core is novel for nickel. The η^2-bound C(1)−S(11) and C(2)−S(21) distances of 1.673(7) and 1.661(7) Å are significantly shorter than the corresponding values in **2**. This result is likely a consequence of the dipositive charge in the trimer that leads to decreased backbonding. The bond lengths for Ni(3)−S(22) and Ni(3)−S(12) of 2.235(2) and 2.238(2) Å, respectively, indicate strong dative interactions from the lone pairs on sulfur and the electrophilic Ni(3). The geometries of all three nickel atoms in this 48 valence electron trimer are approximately square planar.

Reaction of carbon dioxide (Ni:CO_2 = 1:1) with a cold toluene solution of [(dtbpe)Ni]$_2(\eta^2,\mu$-C_6H_6) (**1**)[9] results in loss of benzene and formation of (dtbpe)Ni(η^2-CO_2) (**4**) as a yellow microcrystalline powder that can be conveniently recrystallized from THF/hexanes in good yield (Scheme 2). Complex **4** exhibits ^{1}H and ^{31}P NMR spectroscopic features similar to those of **2** (see also Supporting Information), and its infrared spectrum features a strong ν_{CO} band at 1724 cm^{-1} that corresponds closely to that previously reported for (PCy$_3$)$_2$Ni(CO_2) (1740 cm^{-1}).[5]

The solid-state structure of **4** is shown in Figure 3 (see also Supporting Information). The O(1)−C(3) bond length of 1.266(3) Å is similar to that in (PCy$_3$)$_2$Ni(CO_2) (1.22(2) Å), indicative of strong backbonding. The Ni center is slightly distorted from planarity with the sum of angles about nickel

(15) (a) Baird, M. C.; Wilkinson, G. *J. Chem. Soc. A* **1967**, 865–872. (b) Bianchini, C.; Ghilardi, C. A.; Meli, A.; Midollini, S.; Orlandini, A. *J. Chem. Soc., Chem. Commun.* **1983**, 753–754.
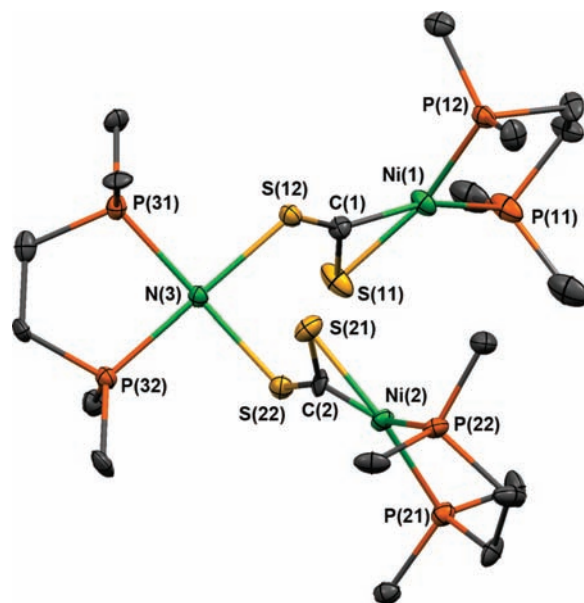

Figure 2. A perspective view of the structure of the complex dication of **3-OTf** with H atoms, and the CH$_3$ groups of the dtbpe ligands omitted for clarity. Thermal ellipsoids are drawn at 35% probability. Selected distances (Å) and angles (°): Ni(3)−S(22) = 2.235(2), Ni(3)−S(12) = 2.238(2), C(2)−S(21) = 1.661(7), C(1)−S(11) = 1.673(7), Ni(2)−C(2) = 1.834(7), Ni(2)−S(21) = 2.144(2), Ni(1)−C(1)=1.858(7), Ni(1)−S(11) = 2.154(2), S(22)−Ni(3)−S(12) = 88.53(7), S(22)−Ni(3)−P(32) = 91.26(8), S(12)−Ni(3)−P(31) = 91.35(7), P(32)−Ni(3)−P(31) = 89.82(8), S(21)−C(2)−S(22) = 134.1(5), S(12)−C(1)−S(11) = 137.3(5), C(1)−Ni(1)−S(11) = 48.6(2), and C(2)−Ni(2)−S(21) = 48.6(2).

∼366°; a small O(1)−Ni-C(3) bite angle of 39.20(9)° compares favorably with the corresponding angle of 37° in (PCy$_3$)$_2$Ni(CO_2).[5]
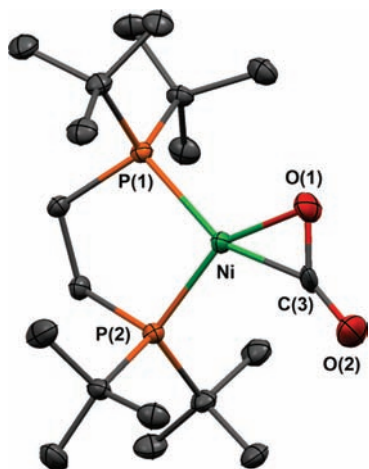
Figure 3. A perspective view of the structure of **4** with H atoms omitted for clarity and thermal ellipsoids drawn at 35% probability. Selected distances (Å) and angles (°): Ni−C(3) = 1.868(2), Ni−O(1) = 1.904(2), O(1)−C(3) = 1.266(3), O(2)−C(3) = 1.200(3), O(2)−C(3)−O(1) = 138.0(2), C(3)−Ni-O(1) = 39.20(9), C(3)−Ni-P(2) = 111.79(8), O(1)−Ni-P(1) = 116.23(5), and P(2)−Ni-P(1) = 92.80(3).

Scheme 2. Formation of a CO_2 Complex of Nickel and Its Thermal Deoxygenation to Give CO
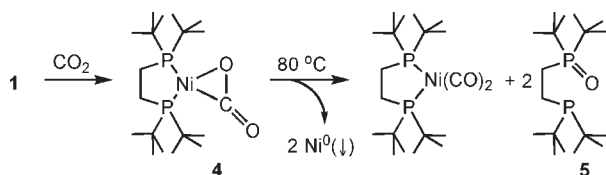
During the synthesis of **4** and attempts to optimize its yield, we noticed that employing an excess of CO_2 or higher temperatures resulted in a complex mixture of products that contained singly oxidized dtbpe. In order to determine whether reduction of CO_2 was occurring, a controlled thermolysis (80 °C, C_6D_6) of **4** was carried out on an NMR-tube scale and monitored by ^{31}P NMR spectroscopy. Over the

course of several days, the resonance corresponding to pure **4** weakened in intensity, and resonances for two new compounds, a singlet and a pair of doublets, appeared in a ∼1:2 ratio, with concomitant precipitation of metallic nickel. These new resonances were assigned to $(dtbpe)Ni(CO)_2$ and singly oxidized dtbpe, O=P(*tert*-Bu)$_2$CH$_2$CH$_2$P(*tert*-Bu)$_2$ (**5**; Scheme 2) by comparison with authentic samples prepared by other routes.[12,16] Thus, the CO_2 ligand in **4** is being reduced to CO with dtbpe serving as the reductant/O atom acceptor. A similar reduction of CO_2 to CO at a nickel center was observed for $[MeC(CH_2PPh_2)_3]Ni(CO_2)$ generated in situ, where a tripodal phosphine served as an oxygen acceptor.[17] Attempts to use other sacrificial reductants to facilitate the deoxygenation of **4** without concurrent oxidation of the dtbpe ligand have not been successful.

Conclusions

The bulky, chelating bis(phosphine) dtbpe (dtbpe = 1,2-bis(di-*tert*-butylphosphino)ethane) provides an excellent platform for stabilizing CS_2 and CO_2 complexes of nickel(0). In the case of CS_2, attempts to prepare odd-electron Ni(I) CS_2 complexes led to disproportionation of the Ni(I) intermediate to give a trimeric, dicationic Ni(0)/Ni(II) coordination complex. The CO_2 complex was thermally unstable with respect to C−O bond cleavage and formed $(dtbpe)Ni(CO)_2$ and singly oxidized dtbpe=O upon heating. The reduction of CO_2 to CO is interesting, but other suitable reductants (O-atom acceptors) have not been found to effect this transformation.

Supporting Information Available: X-ray crystallographic data for **2**, **3-OTf**, and **4** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

(16) A clean sample of O=P(*tert*-Bu)$_2$CH$_2$CH$_2$P(*tert*-Bu)$_2$ was prepared by O$_2$ oxidation of **1**, as described in the Experimental Section.

(17) Bianchini, C.; Mealli, C.; Meli, A.; Sabat, M. *Inorg. Chem.* **1984**, *23*, 2731−2732.