# Synthesis, Structure, and Reactivity of the Ruthenium(VI)−Nickel(II) Complex (dppe)Ni($\mu_3$-S)$_2${Ru(N)Me$_2$}$_2$

Jesse L. Kuiper,[†] Patricia A. Shapley,[*,†] and Christopher M. Rayner[‡]

*Departments of Chemistry, University of Illinois, 601 South Goodwin Avenue, Urbana, Illinois 61801, and University of Leeds, Leeds LS2 9JT, U.K.*

*Received December 16, 2003*

The reaction between Ni(dppe)(SSiMe$_3$)$_2$ and 2 equiv of [N(*n*-Bu)$_4$][Ru(N)Cl$_2$Me$_2$] produces ClSiMe$_3$ and the heterometallic complex (dppe)Ni($\mu_3$-S)$_2${Ru(N)Me$_2$}$_2$. The molecular structure of this complex shows the three metals and the two nitrido ligands in a plane with the bridging sulfur atoms above and below that plane. There is an interaction between one of the ruthenium centers and the nickel. The structure differs from that of the closely related complex (dppe)Pt($\mu_3$-S)$_2${Ru(N)Me$_2$}$_2$, which has equivalent Pt−Ru distances and no strong metal−metal interactions. The complexes (dppe)M($\mu_3$-S)$_2${Ru(N)Me$_2$}$_2$ (M = Pt, Pd, Ni) catalyze the oxidation of benzyl alcohol to benzaldehyde in toluene and in supercritical carbon dioxide.



Heterometallic oxidation catalysts may have improved selectivity over monometallic complexes if the metals act cooperatively.[1] For example, bimetallic ruthenium−platinum complexes can act as catalysts for the electrooxidation of methanol,[2] and a ruthenium−rhodium complex is more active in the oxidation of secondary alcohols with 2-butanone than bimetallic ruthenium complexes or monometallic complexes of either metal.[3] We showed that alcohols are selectively and catalytically oxidized by [N(*n*-Bu)$_4$][Os(N)R$_2$($\mu$-O)$_2$CrO$_2$] and [N(*n*-Bu)$_4$][Ru(N)R$_2$($\mu$-O)$_2$CrO$_2$] (R = Me, CH$_2$SiMe$_3$, Ph) with molecular oxygen.[4] Methanol is oxidized by O$_2$ in the presence of the heterometallic complex (dppe)Pt($\mu_3$-S)$_2${Ru(N)Me$_2$}$_2$.[5]

Supercritical carbon dioxide (scCO$_2$) is gaining popularity as an alternative solvent for oxidation reactions because of its stability to oxidants, tunability, ability to homogenize catalysts, substrates, and light gases (which are infinitely miscible with scCO$_2$), and low environmental impact. Catalytic oxidations in scCO$_2$ media are known and have been the subject of recent reviews.[6] These can use H$_2$O$_2$,[7] *tert*-butyl hydroperoxide,[8,9] or molecular oxygen as the secondary oxidant.[10] Many catalytic oxidation reactions in scCO$_2$ show improved selectivity and yield over the reactions in organic solvents.[9]

Sulfido ligands are particularly useful as bridging units in heterometallic complexes. Because the sulfur atoms are electron-rich and easily polarizable, they bond strongly with both early and late transition metals in a wide range of oxidation states.[11] Many of the rational syntheses of heteronuclear compounds with bridging sulfido ligands involve displacing a ligand on a metal center with a terminal sulfido ligand on another metal.[12] Sulfido ligands can also react directly with some substrates.[13]

We prepared the trimetallic complexes [N(*n*-Bu)$_4$][{Os(N)(CH$_2$SiMe$_3$)$_2$}$_3$($\mu_3$-S)$_2$] and [PPh$_4$][{Ru(N)(CH$_3$)$_2$}$_3$($\mu_3$-S)$_2$][14] and recently demonstrated a general and efficient method for the synthesis of the heterotrimetallic complexes (dppe)M($\mu_3$-S)$_2${Ru(N)Me$_2$}$_2$ (M = Pt, Pd) by the condensation of [Ru(N)Me$_2$Cl$_2$]$^-$ with M(dppe)-

* To whom correspondence should be addressed. E-mail: pshapley@uiuc.edu.
† University of Illinois.
‡ University of Leeds.

(1) (a) Stephan, D. W. *Coord. Chem. Rev*. **1989**, *95*, 41−107. (b) Kovacs, J. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 1131−1133. (c) Dobbs, D. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 6908−6909. (d) Hostetler, M. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 8621−8623. (e) Casey, C. P.; Rutter, E. D., Jr.; Haller, K. J. *J. Am. Chem. Soc.* **1987**, *109*, 6886−6887. (f) Brunner, H.; Challet, S.; Kubicki, M. M.; Leblanc, J.-C.; Moise, C.; Volpato, F.; Wachter, J. *Organometallics* **1995**, *14*, 6323−6324. (g) Massa, M. A.; Rauchfuss, T. B.; Wilson, S. R. *Inorg. Chem.* **1991**, *30*, 4667−4669. (h) Mathur, P.; Hossain, M. M.; Umbarkar, S. B.; Rheingold, A. L.; Liable-Sands, L. M.; Yap, G. P. A. *Organometallics* **1996**, *15*, 1898−1904.

(2) Tess, M. E.; Hill, P. L.; Torraca, K. E.; Kerr, M. E.; Abboud, K. A.; McElwee-White, L. *Inorg. Chem.* **2000**, *39*, 3942−3944.

(3) da Silva, A. C.; Piotrowski, H.; Mayer, P.; Polborn, K.; Severin, K. *Eur. J. Inorg. Chem.* **2001**, 685−691.

(4) Shapley, P. A.; Zhang, N.; Allen, J. L.; Pool, D. H.; Liang, H. C. *J. Am. Chem. Soc.* **2000**, *122*, 1079−1091.

(5) Liang, H. C. Ph.D. Thesis, University of Illinois, Urbana, IL, 1997.

(6) (a) Musie, G.; Wei, M.; Subramaniam, B.; Busch, D. H. *Coord. Chem. Rev.* **2001**, *219*, 789−820. (b) Sahle-Demessie, E.; Gonzalez, M. A.; Enriquez, J.; Zhao, Q. M. *Ind. Eng. Chem. Res.* **2000**, *39*, 4858−4864.

(7) (a) Hancu, D.; Green, J.; Beckman, E. J. *Acc. Chem. Res.* **2002**, *35*, 757−764. (b) Campestrini, S.; Tonellato, U. *Adv. Synth. Catal.* **2001**, *343*, 819−825.

(8) Haas, G. R.; Kolis, J. W. *Organometallics* **1998**, *17*, 4454−4460.

(9) Oakes, R. S.; Clifford, A. A.; Bartle, K. D.; Petti, M. T.; Rayner, C. M. *Chem. Commun.* **1999**, 247−248.

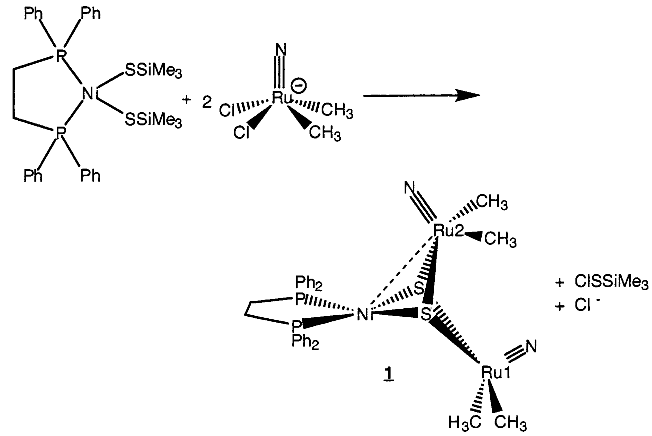
(10) (a) Glaser, R.; Jos, R.; Williardt, J. *Top. Catal.* **2003**, *22*, 31−39. (b) Bolm, C.; Palazzi, C.; Francio, G.; Leitner, W. *Chem. Commun.* **2002**, 1588−1589. (c) Musie, G. T.; Wei, M.; Subramaniam, B.; Busch, D. H. *Inorg. Chem.* **2001**, *40*, 3336−3341. (d) Jenzer, G.; Schneider, M. S.; Wandeler, R.; Mallat, T.; Baiker, A. *J. Catal.* **2001**, *199*, 141−148.

(11) (a) Matsubara, K.; Inagaki, A.; Tanaka, M.; Suzuki, H. *J. Am. Chem. Soc.* **1999**, *121*, 7421−7422. (b) Voss, E. J.; Stern, C. L.; Shriver, D. F. *Inorg. Chem.* **1994**, *33*, 1087−1093. (c) Adams, R. D.; Qu, X.; Wu, W. *Organometallics* **1993**, 4117−4122.

(12) (a) Seino, H.; Arai, Y.; Iwata, N.; Nagao, S.; Mizobe, Y.; Hidai, M. *Inorg. Chem.* **2001,** *40*, 1677−1682. (b) Ikada, T,; Kuwata, S.; Mizobe, Y.; Hidai, M. *Inorg. Chem.* **1998**, *37*, 5793−5797.

10.1021/om034373v CCC: $27.50 
Publication on Web 06/26/2004

**Scheme 1**




$(SSiMe_3)_2$.[15] Here we report the synthesis of the ruthenium−nickel analogue by this method. We also compare the structure and reactivity of this complex to those of the other complexes in this series. The three complexes (dppe)M($\mu_3$-S)$_2${Ru(N)Me$_2$}$_2$ (M = Pt, Pd, Ni) oxidize alcohols in toluene and in $scCO_2$ media.

## Results

The reaction between Ni(dppe)$(SSiMe_3)_2$ and 2 equiv of [N($n$-Bu)$_4$][Ru(N)Cl$_2$Me$_2$] produces the heterometallic complex (dppe)Ni($\mu_3$-S)$_2${Ru(N)Me$_2$}$_2$ (**1**) in greater than 71% yield (Scheme 1). Complex **1** is a burgundy crystalline solid that is moderately soluble in methylene chloride, acetonitrile, toluene, and benzene. It is only slightly soluble in THF and insoluble in diethyl ether, hexane and water. Complex **1** is more soluble in organic solvents than (dppe)Pd($\mu_3$-S)$_2${Ru(N)Me$_2$}$_2$ (**2**) and (dppe)Pt($\mu_3$-S)$_2${Ru(N)Me$_2$}$_2$ (**3**). It is air stable and is stable to water over short time periods.

The $^1$H NMR spectrum shows that the two ruthenium centers in **1** are inequivalent. There are two peaks at 1.62 and 1.15 ppm corresponding to the methyl protons on Ru1 and Ru2, one broad multiplet at 2.33 ppm corresponding to the ethylene protons of the dppe ligand, and three multiplets between 7 and 8 ppm corresponding to the phenyl protons on the dppe ligand. The $^{31}$P NMR spectrum has a single peak at 63.8 ppm, indicating that the two phosphorus atoms in the dppe ligand are equivalent. There are two peaks at 9.9 and 0.0 ppm in the $^{13}$C NMR spectrum for the methyl groups on Ru1 and Ru2. The $^{13}$C NMR spectrum also contains peaks at 4.5 ppm, for the ethylene bridge of the dppe ligand, and six peaks between 133.4 and 129.1 ppm, for the phenyl rings of the dppe ligand. The elemental analysis is consistent with the molecular formulation. There are bands in the IR spectrum at 1066 and 1059 (sh) cm$^{-1}$ for the ruthenium nitrido stretching vibrations.

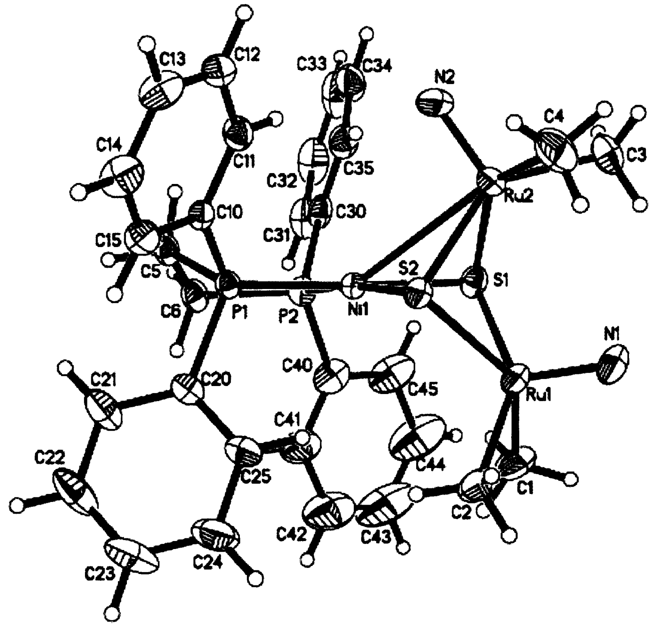



**Figure 1.** ORTEP drawing of complex **1**.

**Table 1. Selected Bond Distances (Å) and Angles (deg) for (dppe)Ni($\mu_3$-S)$_2${Ru(N)Me$_2$}$_2$**

| | | | |
|---|---|---|---|
| Ru1-N1 | 1.600 (4) | Ru1−S1 | 2.3908 (14) |
| Ru2−N2 | 1.598 (5) | Ru1−S2 | 2.3997 (13) |
| Ru1−Ni1 | 3.1194 (8) | Ru2−S1 | 2.3957 (15) |
| Ru2−Ni1 | 2.9011 (8) | Ru2−S2 | 2.4012 (14) |
| Ni1−S1 | 2.2119 (14) | Ni1−S2 | 2.2060 (14) |
| N1−Ru1−S1 | 109.96 (18) | S1−Ni1−P1 | 176.95 (5) |
| N1−Ru1−S2 | 113.67 (16) | S1−Ni1−P2 | 90.63 (5) |
| N2−Ru2−S1 | 110.8 (2) | S2−Ni1−P1 | 95.65 (5) |
| N2−Ru2−S2 | 114.42 (17) | Ru2−Ni1−P1 | 125.92 (4) |
| Ru1−S1−Ni1 | 85.37 (5) | Ru2−S1−Ni1 | 78.04 (4) |
| Ru1−S2−Ni1 | 85.02 (4) | Ru2−S2−Ni1 | 77.82 (4) |

We determined the molecular structure of **1**·$CH_2Cl_2$ by X-ray crystallography. Figure 1 shows the ORTEP diagram with the $CH_2Cl_2$ molecule removed for clarity. The ruthenium centers have a distorted-square-pyramidal geometry with the nitrido ligand in the apical position. The ruthenium is above the plane of the four other ligands, two methyl ligands, and two $\mu$-sulfido ligands. The nickel center has a distorted-square-planar geometry. One ruthenium center, Ru2, is within bonding distance to the nickel center at 2.901(8) Å. The other ruthenium center, Ru1, is more distant at 3.119(8) Å from the nickel. The four ruthenium−sulfur bond distances are very similar, ranging between 2.3908(14) and 2.4012(14) Å. Table 1 shows selected bond distances and angles of complex **1**.

Complex **1** reacts very slowly with triphenylphosphine to give 1 equiv of triphenylphosphine sulfide and an as yet unidentified phosphine complex. It does not react with molecular oxygen or hydrogen peroxide.

The complexes (dppe)M($\mu_3$-S)$_2${Ru(N)Me$_2$}$_2$ (M = Pt, Pd, Ni) catalyze the oxidation of benzyl alcohol to benzaldehyde with molecular oxygen. We compared the oxidation of benzyl alcohol with $O_2$ in the presence of catalytic amounts of **1**−**3** in a typical organic solvent, toluene, and in a more environmentally friendly solvent, supercritical $CO_2$. Optimal conditions in $scCO_2$ are 18.8 bar of 20% $O_2$ (3.36 mmol), with 120 bar total pressure. The concentration of catalyst was $5.06 \times 10^{-4}$ M, and the temperature was 100 °C for each reaction. Table 2

(13) (a) Birnbaum, J.; DuBois, M. R. *Organometallics* **1994**, *13*, 1014−1019. (b) Koval, C. R.; Lopez, L. L.; Kaul, B. B.; Renshaw, S.; Green, K.; DuBois, M. R. *Organometallics* **1995**, *14*, 3440−3447. (c) Kaul, B. B.; Noll, B.; Renshaw, S.; DuBois, M. R. *Organometallics* **1997**, *16*, 1604−1611. (d) DuBois, M. R.; Vasquez, L. D.; Ciancanelli, R. F.; Noll, B. C. *Organometallics* **2000**, *19*, 3507−3515. (e) Vasquez, L. D.; Noll, B. C.; DuBois, M. R. *Inorg. Chem.* **2001**, *40*, 1391−1393.

(14) Shapley, P. A.; Liang, H.-C.; Shusta, J. M.; Schwab, J. J.; Zhang, N.; Wilson, S. R. *Organometallics* **1994**, *13*, 3351−3359.

(15) Shapley, P. A.; Liang, H. C.; Dopke, N. C. *Organometallics* **2001**, *20*, 4700−4704.

**Table 2. Catalytic Oxidation of Benzyl Alcohol to Benzaldehyde by $O_2$ at 100 °C**

| catalyst | solvent | pressure (bar) | TON | TOF ($h^{-1}$) | time (h) | conversn (%) |
|---|---|---|---|---|---|---|
| **1** | toluene | 2.8 ($O_2$) | 18.45 | 0.77 | 24 | 53 |
| **2** | toluene | 2.8 ($O_2$) | 3.63 | 0.15 | 24 | 32 |
| **3** | toluene | 2.8 ($O_2$) | 7.06 | 0.29 | 24 | 35 |
| **1** | $CO_2$ | 120 (total) 10 ($O_2$) | 9.57 | 0.48 | 20 | 19 |
| **2** | $CO_2$ | 120 (total) 10 ($O_2$) | 9.18 | 0.46 | 20 | 18 |
| **3** | $CO_2$ | 120 (total) 10 ($O_2$) | 5.97 | 0.30 | 20 | 11 |
| **3** | $CO_2$ | 100 (total) 10 ($O_2$) | 5.15 | 0.26 | 20 | 10 |
| **3** | $CO_2$ | 80 (total) 10 ($O_2$) | 4.79 | 0.24 | 20 | 10 |
| **3** | $CO_2$ | 120 (total) 18.8 ($O_2$) | 15.99 | 0.80 | 20 | 32 |
| **3** | $CO_2$ | 120 (total) 44 ($O_2$) | 10.70 | 0.54 | 20 | 22 |
| **3** | $CO_2/CH_2Cl_2$ | 100 (total) 10 ($O_2$) | 1.96 | 0.10 | 20 | 4 |



shows the turnover numbers for the oxidation of benzyl alcohol under various conditions.

Under the same conditions used for the oxidation of benzyl alcohol above, complexes **1**−**3** do not oxidize 1-hexene, cyclohexene, or cyclooctene. They slowly oxidize the unsaturated alcohol, geraniol, only at the hydroxy group to form citral with a turnover number for **1** of 7.0, for **2** of 5.0, and for **3** of 4.4 after 24 h.

## Discussion

The trimethylsilanethiolate complexes of platinum(II), palladium(II), and nickel(II) are useful precursors to heterometallic complexes with $\mu$-sulfido linkages. The synthesis of the heterometallic complexes (dppe)M($\mu_3$-S)$_2${Ru(N)Me$_2$}$_2$ (M = Ni, Pd, Pt) by reaction of M(dppe)(SSiMe$_3$)$_2$ with 2 equiv of [N(*n*-Bu)$_4$][Ru(N)Cl$_2$Me$_2$] generates the heterometallic complexes, 2 equiv of chlorotrimethylsilane, and 2 equiv of tetra-*n*-butylammonium chloride. Formation of the stronger Si−Cl bond (Si−Cl, 91 kcal/mol; Si−S, 70 kcal/mol) and removal of the volatile compound chlorotrimethylsilane drive the reaction.

A single-crystal X-ray diffraction analysis shows that complex **1** resembles (dppe)Pt($\mu_3$-S)$_2${Ru(N)Me$_2$}$_2$ in the local geometry around each metal center.[14] In both complexes, the ruthenium centers have a distorted-square-pyramidal geometry and the nickel/platinum center has a distorted-square-planar geometry. The three metals are bridged by $\mu$-sulfido ligands, and the nitrido ligands are in the plane of the metals.

The key difference between the molecular structures of (dppe)Ni($\mu_3$-S)$_2${Ru(N)Me$_2$}$_2$ and (dppe)Pt($\mu_3$-S)$_2${Ru(N)Me$_2$}$_2$ is the variance in Ru−Ni bond distances versus Ru−Pt bond distances. In (dppe)Pt($\mu_3$-S)$_2${Ru(N)Me$_2$}$_2$, the two Ru−Pt distances are equivalent and the length is somewhat greater than a typical single bond. In contrast, the two Ru−Ni bond distances in (dppe)Ni($\mu_3$-S)$_2${Ru(N)Me$_2$}$_2$ are different by more than 0.2 Å. The short Ru−Ni distance may be due to a weak two-electron interaction of the $p_z$ orbital on the electron-poor nickel center with the electron-rich $d_{xy}$ orbital on Ru2 in order to achieve an 18e count on the nickel center. The nickel in complex **1** has a smaller HOMO−LUMO gap than the platinum or palladium in the analogous complexes, allowing for a weak interaction of the empty $p_z$ orbital of the nickel complex with the ruthenium $d_{xy}$ orbital.

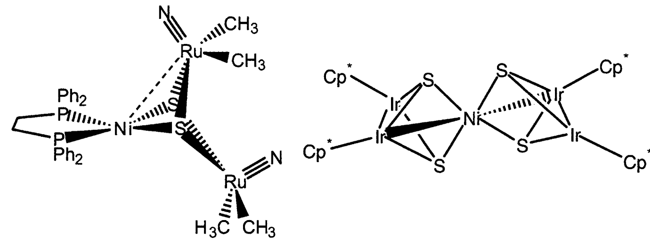



**Figure 2.** Comparison of (dppe)Ni($\mu_3$-S)$_2${Ru(N)Me$_2$}$_2$ and [(Cp*Ir)$_2$($\mu_3$-S)$_2$Ni($\mu_3$-S)$_2$(IrCp*)$_2$]$^+$.

Complex **1** has a Ru2−Ni distance that is 0.2−0.4 Å longer than typical ruthenium−nickel heterometallic complexes with covalent single bonds,[16] indicating a dative bond.[17] This bond is not a result of steric interactions. Although the Ni−S bonds are on average 0.2 Å shorter than in the platinum complex, this change is not enough to bring the methyl ligands on Ru1 and the phenyl substituents on the dppe ligand on nickel into contact. The closest distance between these substituents is well over 3 Å, for C2 to C24. Hidai and coworkers reported a similar interaction in the heterometallic cation [{(Cp*Ir)$_2$($\mu_3$-S)$_2$}$_2$Ni]$^+$.[18] The Ni−S bond distances in (dppe)Ni($\mu_3$-S)$_2${Ru(N)Me$_2$}$_2$ and [{(Cp*Ir)$_2$($\mu_3$-S)$_2$}$_2$Ni]$^+$ are nearly the same.[19] The Ru2−Ni dative bond distance in complex **1** is longer than the Ir−Ni distance in Hidai's complex, showing a somewhat weaker interaction.

Supercritical $CO_2$ behaves as a nonpolar organic solvent with respect to substrates and catalysts. The complexes (dppe)M($\mu_3$-S)$_2${Ru(N)Me$_2$}$_2$ (M = Pt, Pd, Ni) are not soluble in pure sc$CO_2$, but they are soluble in the mixture of sc$CO_2$ and benzyl alcohol. Cosolvents are useful in solubilizing transition-metal complexes in supercritical $CO_2$ for catalytic oxidation reactions.[20] In this case, the reactant is the cosolvent.

Increasing the overall pressure by adding $CO_2$ to the reaction mixture resulted in increased turnovers. Increasing the amount of $CO_2$ in the reactor increases the density of the sc$CO_2$, thereby enhancing the solvation power of sc$CO_2$ with respect to the heterometallic complexes. Several reports from the Leeds group have shown that variation of $CO_2$ pressure has profound effects on the reactions carried out in this solvent.[21,22]

Oxygen concentration also affects the turnover number. Increasing the $O_2$ partial pressure from 10 to 18.8

(16) (a) Lanfranchi, M.; Tiripicchio, A.; Sappa, E.; MacLaughlin, S. A.; Carty, A. J. *J. Chem. Soc., Chem. Commun.* **1982**, 538−539. (b) Lanfranchi, M.; Tiripicchio, A.; Camellini, M. T.; Gambino, O.; Sappa, E. *Inorg. Chim. Acta* **1982**, *64*, L269-L271.

(17) Tang, Z.; Nomura, Y.; Kuwata, S.; Ishii, Y.; Mizobe, Y.; Hidai, M. *Inorg. Chem.* **1998**, *37*, 4909−4920.

(18) Tang, Z.; Nomura, Y.; Kuwata, S.; Ishii, Y.; Mizobe, Y.; Hidai, M. *Inorg. Chem.* **1998**, *37*, 4909−4920.

(19) (a) Do, Y.; Simhon, E. D.; Holm, R. H. *Inorg. Chem.* **1983**, *22*, 3809−3812. (b) Matsumoto, K.; Saiga, N.; Tanaka, S.; Ooi, S. *J. Chem. Soc., Perkin Trans. 1* **1991**, 1265−1271.

(20) Wei, M.; Musie, G. T.; Busch, D. H.; Subramaniam, B. *J. Am. Chem. Soc.* **2002,** *124*(11), 2513−2517.

(21) (a) Oakes, R. S.; Clifford, A. A.; Rayner, C. M. *J. Chem. Soc., Perkin Trans. 1* **2001**, 917−941. (b) Oakes, R. S.; Heppenstall, T. J.; Shezad, N.; Clifford, A. A.; Rayner, C. M. *Chem. Commun.* **1999**, 1459−1460.

(22) Rose, P. M.; Clifford, A. A.; Rayner, C. M. *Chem. Commun.* **2002**, 968.

bar increases the turnover number, but further increases in the oxygen partial pressure do not increase oxidation of benzyl alcohol. At high oxygen partial pressure the benzyl alcohol and oxygen may be competing for a binding site on the heterometallic complex. We see a similar effect with the heterometallic catalyst [*n*-$Bu_4N$][Os(N)($CH_2SiMe_3$)$_2$($\mu$-O)$_2CrO_2$].[5] Increased oxygen concentration necessarily decreases $CO_2$ concentration, which leads to lower catalyst and substrate solubility.

Benzyloxy complexes of osmium(VI) and ruthenium(VI), [$NBu_4$][M(N)($OCH_2Ph$)$_4$], produce equal quantities of benzaldehyde and benzyl alcohol through $\beta$-hydrogen elimination followed by reductive elimination.[23] The heterometallic osmium(VI) and ruthenium(VI) complexes [*n*-$Bu_4N$][M(N)($CH_2SiMe_3$)$_2$($\mu$-O)$_2CrO_2$] catalyze the oxidation of benzyl alcohol to benzaldehyde through a mechanism that involves $\beta$-hydrogen elimination of an intermediate alkoxide complex. It is likely that benzyl alcohol reacts with (dppe)Ni($\mu_3$-S)$_2${Ru(N)$Me_2$}$_2$ to form an intermediate ruthenium benzyloxy complex that also eliminates a methylene hydrogen to the cluster and releases the product aldehyde.

There were no significant changes in product distribution or reaction rates for the oxidation of benzyl alcohol in toluene as opposed to sc$CO_2$. Although molecular oxygen is more soluble in sc$CO_2$ than in toluene, the organometallic complexes are much more soluble in the organic solvent. Heterometallic complexes with longer chain alkyl groups bonded to ruthenium or on the phosphine ligand should be more soluble in sc$CO_2$ and have improved activity in that solvent.

## Conclusion

We have completed the synthesis and characterization of the series of heterometallic complexes {M(dppe)}($\mu_3$-S)$_2${Ru(N)$Me_2$}$_2$, where M = Pt, Pd, Ni. Unlike {Pt(dppe)}($\mu_3$-S)$_2${Ru(N)$Me_2$}$_2$, {Ni(dppe)}($\mu_3$-S)$_2$-{Ru(N)$Me_2$}$_2$ has a close Ru−Ni interaction, indicating a weak, dative bond between those metals. The three heterometallic complexes are similar in their ability to oxidize benzyl alcohol with molecular oxygen, but the nickel-substituted complex is slightly more active than the palladium and platinum analogues. The product distribution and reaction rates for the oxidation of benzyl alcohol in toluene are similar to those oxidations in supercritical carbon dioxide.

## Experimental Section

**General Synthetic Conditions.** All reactions were conducted under an $N_2$ atmosphere using standard air-sensitive techniques in a Vacuum Atmospheres glovebox unless otherwise stated. Anhydrous diethyl ether and hexane were distilled from Na/benzophenone. Methylene chloride was distilled from $CaH_2$, and toluene was distilled from Na. The compounds $NaSSiMe_3$,[24] Ni(dppe)($SSiMe_3$)$_2$, [N(*n*-Bu)$_4$][Ru(N)$Cl_2Me_2$], (dppe)Pd($\mu_3$-S)$_2${Ru(N)$Me_2$}$_2$, and (dppe)Pt($\mu_3$-S)$_2${Ru(N)$Me_2$}$_2$ were prepared according to literature methods.[14] Benzyl alcohol and benzaldehyde were purchased from Aldrich and distilled. All NMR spectra were recorded on a Varian Unity-400 FT NMR spectrometer at ambient temperature and referenced to internal solvent at 7.26 ppm. IR spectra were recorded on a Perkin-Elmer 1600 series FTIR. UV−visible spectra were recorded on a Hewlett-Packard 8452A spectrometer. Gas chromatography was performed on an Agilent 6850 CG and analyzed with Agilent Cerity software. All elemental analyses were performed by the University of Illinois microanalytical service.

**Synthesis of {Ni(dppe)}($\mu_3$-S)$_2${Ru(N)$Me_2$}$_2$.** A solution of Ni(dppe)($SSiMe_3$)$_2$ (0.023 g, 0.034 mmol) in 2 mL of $CH_2Cl_2$ was slowly added to a solution of [N(*n*-Bu)$_4$][Ru(N)$Cl_2Me_2$] (0.032 g, 0.069 mmol) in 2 mL of $CH_2Cl_2$ at −30 °C. The purple solution mixture turned dark red. After 12 h at −30 °C, the solution was concentrated under vacuum. The mixture was added to a silica gel chromatography column and eluted with 4/1 *n*-$C_6H_{14}$/$CH_2Cl_2$. The first red band was collected and cooled. Red, needlelike crystals formed (0.020 g, 0.025 mmol, 71%). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.99−7.27 (m, 20 H, P$C_6H_5$), 2.36−2.31 (m, 4 H, P$CH_2$), 1.62 (s, 6 H, $Ru_aCH_3$), 1.15 (s, 6 H, $Ru_bCH_3$). $^{13}C$ NMR (125.7 MHz, $CDCl_3$): $\delta$133.5−129.1 (m, P($C_6H_5$)$_3$, 10.0 ($Ru_aCH_3$), 4.5 ($PCH_2CH_2P$), −0.2 ($Ru_bCH_3$) $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$): $\delta$ 63.8 (s). UV−visible ($\epsilon$): 236 nm (30 543.9), 276 nm (19 383.2), 394 nm (3362.6). IR (KBr pellet; cm$^{-1}$): 478, 525, 691, 741, 810, 873, 1063 ($\nu$(Ru(N))), 1100 ($\nu$(Ru(N))), 1177, 1431, 2892 ($\nu$(CH)), 2964 ($\nu$(CH)). Anal. Calcd for $C_{30}H_{36}N_2NiP_2Ru_2S_2\cdot{}^1/_3CH_2Cl_2$: C, 43.38; H, 4.40; N, 3.34. Found: C, 43.49; H, 4.51; N, 3.23.

**Reaction of (dppe)Ni($\mu_3$-S)$_2${Ru(N)$Me_2$}$_2$ with $O_2$.** In a thick-walled reaction tube, 5 mg (0.006 mmol) of (dppe)Ni-($\mu_3$-S)$_2${Ru(N)$Me_2$}$_2$ was dissolved in 1 mL of $CDCl_3$. The tube was pressurized to 40 psi of $O_2$ and heated to 60 °C for 3 days. A $^1H$ NMR spectrum showed only starting material.

**Reaction of (dppe)Ni($\mu_3$-S)$_2${Ru(N)$Me_2$}$_2$ with $H_2O_2$.** In an NMR tube, 11 mg (0.014 mmol) of (dppe)Ni($\mu_3$-S)$_2${Ru(N)-$Me_2$}$_2$ was dissolved in 0.75 mL of $CDCl_3$. To this tube was added 1 equiv of 30% $H_2O_2$ solution (1.6 $\mu$L, 0.014 mmol) in water. A $^1H$ NMR spectrum after 16 h showed only starting material.

**Reaction of (dppe)Ni($\mu_3$-S)$_2${Ru(N)$Me_2$}$_2$ with $PPh_3$.** In an NMR tube, 8 mg (0.10 mmol) of (dppe)Ni($\mu_3$-S)$_2${Ru(N)$Me_2$}$_2$ was dissolved in 0.75 mL of $CDCl_3$. To this tube was added 1 equiv of $PPh_3$ (3 mg, 0.010 mmol). A $^1H$ NMR spectrum acquired after 16 h showed **1** and a new organometallic compound in equal amounts. $^1H$ NMR (400 MHz, $CDCl_3$, 23.2 °C): $\delta$ 7.98−7.46 (m, 20H, P$C_6H_5$), 7.36−7.28 (m, 36.6 H $PPh_3$ *H*), 2.35−2.26 (m, 4.02 H, $PCH_2CH_2P$), 1.61 (s, 5.85 H, $Ru_aCH_3$), 1.14 (s, 6.10 H, $Ru_bCH_3$). $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$, 23.2 °C): $\delta$ 63.8 (s). $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$, 23.2 °C): $\delta$ 65.1 (s), 63.9 (s, $CH_2P(Ph)_2Ni$), 60.2 (s), 46.4 (s, S=$PPh_3$), 39.1 (s), 32.1 (s), −2.2 (s, $PPh_3$).

**Oxidations of Benzyl Alcohol, Geraniol, and Cyclooctene by 1−3 in Toluene.[25]** Solutions were prepared by dissolving nonane (17 $\mu$L, 0.097 mmol) and **1** (0.044 66 g, 0.055 mmol), **2** (0.083 14 g, 0.050 mmol), or **3** (0.047 36 g, 0.050 mmol) in 10.0 mL of toluene. For oxidation studies, a 1 mL aliquot was placed in a pressure reactor along with substrate (0.11 or 0.25 mmol). An aliquot of the solution was removed for GC analysis. The pressure reactor was flushed with $O_2$ and then pressurized to 2.8 bar (40 psi) of $O_2$ (4.61 mmol) and heated to 100 °C for 24 h. The reaction mixture was cooled to −78 °C, and a sample was analyzed by gas chromatography.

**Oxidations of Benzyl Alcohol, Geraniol, and Cyclooctene by 1−3 in sc$CO_2$.[3]** Solid **1** (0.0093 g, 0.0115 mmol), **2** (0.0106 g, 0.0123 mmol), or **3** (0.0103 g, 0.0109 mmol) was added to a 20 mL pressure reactor along with 50 equiv of substrate. The pressure reactor was sealed and tested for leaks. The reactor was charged with $O_2$ as a 10% or 20% mixture in $CO_2$ and then heated to 100 °C. Once the temper-

(23) Reinerth, W. A.; Shapley, P. A. *Organometallics* **1996**, *15*, 5090−5096.
(24) Do, Y.; Simhon, E. D.; Holm, R. H. *Inorg. Chem.* **1983**, *22*, 3809−3812.

(25) As with all reactions under high pressure, appropriate safety precautions must be taken. See refs 9 and 21 for further information.

**Table 3. Oxidation of Benzyl Alcohol in $scCO_2$: Complex Comparison at 120 bar of $CO_2$**

| | amt (mmol) | | |
|---|---|---|---|
| complex | complex | substrate | oxygen |
| **1** | 0.011 | 0.54 | 0.89 |
| **2** | 0.012 | 0.62 | 0.89 |
| **3** | 0.011 | 0.57 | 0.89 |

**Table 4. Oxidation of Benzyl Alcohol in $ScCO_2$: Total Pressure Comparison**

| | $CO_2$ | amt (mmol) | | |
|---|---|---|---|---|
| complex | pressure (bar) | complex | substrate | oxygen |
| **3** | 80 | 0.011 | 0.54 | 0.89 |
| **3** | 100 | 0.013 | 0.67 | 0.89 |
| **3** | 120 | 0.011 | 0.54 | 0.89 |

**Table 5. Oxidation of Benzyl Alcohol in $ScCO_2$: Oxygen Pressure Comparison at @ 120 Bar $CO_2$**

Oxygen Pressure Comparison at 120 bar of $CO_2$

| | $O_2$ pressure | amt (mmol) | | |
|---|---|---|---|---|
| complex | (bar) | complex | substrate | oxygen |
| **3** | 10 (10%) | 0.011 | 0.54 | 0.89 |
| **3** | 18.8 (20%) | 0.010 | 0.50 | 3.35 |
| **3** | 44 (20%) | 0.010 | 0.51 | 7.86 |

Solvent Expansion

| | amt (mmol) | | |
|---|---|---|---|
| complex | complex | substrate | oxygen |
| **3** | 0.013 | 0.67 | 0.89 |
| **3**, 5 mL of $CH_2Cl_2$ | 0.009 | 0.47 | 0.89 |

ature was stabilized, additional $CO_2$ was added (Tables 3−5). After 20 h at 100 °C, the reactor was cooled and vented into $CH_2Cl_2$ to trap any volatile material. The $CH_2Cl_2$ was removed under vacuum, and the residual oil was combined with the contents of the reactor. The products were analyzed by NMR spectroscopy.

**Structure Determination.** The data crystals of **1** were formed in $CH_2Cl_2/Et_2O$ at −30 °C. Methylene chloride solvate was disordered in two positions. They were mounted using oil (Paratone-N, Exxon) to a thin glass fiber. Data for **1** were collected on a Siemens Platform/CCD automated diffractometer. Systematic conditions suggested the unambiguous space group *Pcba*. The structure was solved by direct methods. Ideal geometry was imposed on the disordered solvate molecule using an effect standard deviation of 0.01%. Displacement parameters for disordered atoms were restrained to similar and rigid-bond values (esd 0.01). Hydrogen atoms were included as riding idealized contributors. Hydrogen atom $U$ values were assigned as 1.2 times the $U_{eq}$ value of adjacent non-H atoms. The space group choice was confirmed by successful convergence of the full-matrix least-squares refinement on $F^2$ (Sheldrick, 2000). The highest peaks in the final difference Fourier map were in the vicinity of metal atoms and the disordered solvate; the final map had no other significant features. A final analysis of variance between observed and calculated structure factors showed no dependence on amplitude or resolution.

**Acknowledgment.** This research has been supported by a grant from the U.S. Environmental Protection Agency's Science to Achieve Results (STAR) program (Grant No. EPA R 829553). We also gratefully acknowledge the financial support of the donors of the Petroleum Research Fund, administered by the American Chemical Society. We thank Prof. Tony Clifford (University of Leeds) for helpful discussions and the Worldwide University Network, University of Illinois, and the University of Leeds for funding an exchange studentship (J.L.K.). NMR spectra were obtained in the Varian Oxford Instrument Center for Excellence in NMR Laboratory. Funding for this instrumentation was provided in part from the W. M. Keck Foundation, the National Institutes of Health (Grant No. PHS 1 S10 RR10444-01), and the National Science Foundation (Grant No. NSF CHE 96-10502). Purchase of the Siemens Platform/CCD diffractometer by the School of Chemical Sciences was supported by National Science Foundation Grant No. CHE 9503145.

**Supporting Information Available:** For **1**, tables of crystal data collection and refinement parameters, bond distances and angles, and anisotropic displacement parameters; these data are also available as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

OM034373V