5952 *Inorg. Chem.* **1994,** *33,* 5952−5954

Notes

Reactivity of $[PPN][Ru_3(\mu\text{-}NO)(CO)_{10}]$ with Tertiary Silanes and Stannanes

Javier A. Cabeza,* R. Jesús Franco, and Víctor Riera

Instituto de Química Organometálica, Facultad de Química,
Universidad de Oviedo, 33071 Oviedo, Spain

Received May 10, 1994

Introduction

The discovery that bis(triphenylphosphino)nitrogen(1+) nitrite, $[PPN]NO_2$, is a useful reagent to introduce nitrosyl ligands in carbonyl cluster complexes[1] has allowed the development of the chemistry of such nitrosyl-containing compounds.[2] In this field, as far as anionic ruthenium carbonyl clusters are concerned, it is known that the complex $[PPN][Ru_3(\mu\text{-}NO)(CO)_{10}]$ (**1**), which can be easily made from $[Ru_3(CO)_{12}]$ and $[PPN]NO_2$,[1] reacts with electrophiles (which attack either at the metal atoms[3−5] or at the nitrosyl oxygen atom[3,4]) and nucleophiles[3,4] (which substitute carbonyl ligands); it also undergoes N−O bond cleavage reactions (leading to isocyanato derivatives or higher nuclearity nitrido clusters);[4] but, however, no oxidative addition reactions have been reported to date.

We now report the reactivity of compound **1** with tertiary silanes and stannanes. We initially used $HSiEt_3$ and $HSnBu_3$ as reagents, but as most of their products were obtained as oils which proved to be very difficult to crystallize, we also carried out the reactions using $HSiPh_3$ and $HSnPh_3$. We undertook this study prompted by the fact that $[PPN][Ru_3(\mu\text{-}H)(\mu\text{-}CO)(CO)_{10}]$, a cluster complex that is isoelectronic with **1**, reacts with tertiary silanes and stannanes to give $[PPN][Ru_3(\mu\text{-}H)(ER_3)_2(CO)_{10}]$ (E = Si, Sn);[6] these compounds (E = Si) are useful catalyst precursors for homogeneously catalysed reactions involving hydrosilanes.[7]

Experimental Section

All reactions were carried out under nitrogen using standard Schlenk techniques and were routinely monitored by solution IR spectroscopy (carbonyl stretching region). Solvents were purified according to standard literature procedures[8] and distilled under nitrogen prior to use. Compound **1** was prepared as described previously[1,9] by Stevens and Gladfelter. ^{13}CO-enriched **1** was prepared similarly starting from ^{13}CO-enriched $[Ru_3(CO)_{12}]$[10] and $[PPN]NO_2$. All other reagents were purchased from Aldrich and used as received. Infrared spectra were recorded in solution on a Perkin-Elmer FT 1720-X spectrophotometer, using 0.1-mm CaF_2 cells. NMR spectra were run with Bruker AC-200 (^{1}H) and AC-300 (^{1}H and ^{13}C) instruments, being referred to internal $SiMe_4$ ($\delta = 0$ ppm). Microanalyses were obtained from the University of Oviedo Analytical Service.

$[PPN][Ru_3(\mu\text{-}NO)(\mu\text{-}H)(SiEt_3)(CO)_9]$ (2a). $HSiEt_3$ (7 μL, 0.047 mmol) was added to a solution of complex **1** (50 mg, 0.043 mmol) in THF (10 mL). The mixture was stirred at reflux temperature for 35 min. The color changed from yellow-brown to dark red. The solvent was removed under reduced pressure to give complex **2a** as a dark red oil, soluble in all organic solvents.

$[PPN][Ru_3(\mu\text{-}NO)(\mu\text{-}H)(SiPh_3)(CO)_9]$ (2b). A solution of complex **1** (50 mg, 0.043 mmol) and $HSiPh_3$ (13 mg, 0.047 mmol) in THF (15 mL) was stirred at reflux temperature for 45 min. The solvent was removed under reduced pressure and the residue washed with hexane (3 × 3 mL) and dried under vacuum to give compound **2b** as a red solid (39 mg, 66%). Anal. Calcd for $C_{63}H_{46}N_2O_{10}P_2Ru_3Si$: C, 54.7; H, 3.3; N, 2.0. Found: C, 54.9; H, 3.4; N, 2.2.

$[PPN][Ru_3(\mu\text{-}NO)(\mu\text{-}H)(SnBu_3)(CO)_9]$ (2c). A solution of complex **1** (50 mg, 0.043 mmol) and $HSnBu_3$ (13 μL, 0.044 mmol) in THF (10 mL) was stirred at room temperature for 30 min. The solvent was removed under reduced pressure to give a dark red oil, soluble in all organic solvents, spectroscopically identified as compound **2c**.

$[PPN][Ru_3(\mu\text{-}NO)(\mu\text{-}H)(SnPh_3)(CO)_9]$ (2d). A solution of complex **1** (66 mg, 0.057 mmol) and $HSnPh_3$ (20 mg, 0.057 mmol) in THF (15 mL) was stirred at room temperature for 1 h. The solvent was removed under reduced pressure, and the residue washed with 3:2 hexane−diethyl ether (5 mL) and dried under vacuum to give compound **2d** as a dark red solid (58 mg, 68%). Anal. Calcd for $C_{63}H_{46}N_2O_{10}P_2Ru_3Sn$: C, 51.3; H, 3.1; N, 1.9. Found: C, 51.9; H, 3.0; N, 1.8. $^{13}C\{^1H\}$ NMR ($CDCl_3$, −60 °C, ^{13}CO-enriched sample): 216.9, 207.3, 206.5, 204.9, 203.2 (2 C), 200.5, 198.8, 186.9 ppm (9 CO ligands).

$[PPN][Ru_3(\mu\text{-}NO)(\mu\text{-}H)_2(SiEt_3)_2(CO)_8]$ (3a). A solution of complex **1** (50 mg, 0.043 mmol) and $HSiEt_3$ (17 μL, 0.108 mmol) in THF (15 mL) was stirred at reflux temperature for 3 h. The solvent was removed under reduced pressure to give complex **3a** as a red oil, soluble in all organic solvents.

$[PPN][Ru_3(\mu\text{-}NO)(\mu\text{-}H)_2(SiPh_3)_2(CO)_8]$ (3b). A solution of complex **1** (50 mg, 0.043 mmol) and $HSiPh_3$ (28 mg, 0.108 mmol) in THF (15 mL) was stirred at room temperature for 1.75 h. The solvent was removed under reduced pressure, and the residue washed with diethyl ether (3 × 3 mL) and dried under vacuum to give compound **3b** as a red-brown solid (43 mg, 62%). Anal. Calcd for $C_{80}H_{62}N_2O_9P_2Ru_3Si_2$: C, 59.4; H, 3.9; N, 1.7. Found: C, 59.8; H, 4.0; N, 1.5.

$[PPN][Ru_3(\mu\text{-}NO)(\mu\text{-}H)_2(SnBu_3)_2(CO)_8]$ (3c). A solution of compound **1** (50 mg, 0.043 mmol) and $HSnBu_3$ (29 mg, 0.108 mmol) in THF (15 mL) was stirred at reflux temperature for 1.75 h. The solvent was removed under reduced pressure to give compound **3c** as a red-brown oil, soluble in all organic solvents. $^{13}C\{^1H\}$ NMR ($CDCl_3$, −60 °C, ^{13}CO-enriched sample): 211.8, 207.2, 205.8, 204.2 (2 C), 203.1, 200.5, 189.4 ppm (8 CO ligands).

$[PPN][Ru_3(\mu\text{-}NO)(\mu\text{-}H)_2(SnPh_3)_2(CO)_8]$ (3d). A solution of complex **1** (50 mg, 0.043 mmol) and $HSnPh_3$ (38 mg, 0.108 mmol) in THF (15 mL) was stirred at room temperature for 1.75 h. The solvent was removed under reduced pressure, and the residue washed with hexane (3 × 3 mL) and dried under vacuum to give compound **3d** as a brown solid (58 mg, 75%). Anal. Calcd for $C_{80}H_{62}N_2O_9P_2Ru_3Sn_2$: C, 53.4; H, 3.5; N, 1.6. Found: C, 53.3; H, 3.6; N, 1.4.

Results

The anionic nitrosyl cluster complex $[PPN][Ru_3(\mu\text{-}NO)(CO)_{10}]$ (**1**) reacted with one equivalent of tertiary silane or

---

(1) Stevens, R. E.; Gladfelter, W. L. *Inorg. Chem.* **1983**, *22*, 2034.

(2) Richter-Addo, G. B.; Legzdins, P. *Metal Nitrosyls*; Oxford University Press: New York, 1992; Chapter 5.

(3) Stevens, R. E.; Guettler, R. D.; Gladfelter, W. L. *Inorg. Chem.* **1990**, *29*, 451.

(4) Stevens, R. E.; Fjare, D. E.; Gladfelter, W. L. *J. Organomet. Chem.* **1988**, *347*, 373.

(5) Gómez-Sal, M. P.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Syed-Mustaffa, S. N. A. B. *J. Organomet. Chem.* **1984**, *272*, C21.

(6) (a) Süss-Fink, G.; Ott, J.; Schmidkonz, B.; Guldner, K. *Chem. Ber.* **1982**, *115*, 2487. (b) Klein, H.-P.; Thewalt, U.; Herrmann, G.; Süss-Fink, G.; Moinet, C. *J. Organomet. Chem.* **1985**, *286*, 225.

(7) (a) Süss-Fink, G.; Reiner, J. *J. Mol. Catal.* **1982**, *16*, 231. (b) Süss-Fink, G. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 73. (c) Süss-Fink, G.; Reiner, J. *J. Organomet. Chem.* **1981**, *221*, C36. (d) Herrmann, G.; Süss-Fink, G. *Chem. Ber.* **1985**, *118*, 3959.

(8) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon Press: Oxford, U.K., 1980.

(9) Stevens, R. E.; Yanta, T. J.; Gladfelter, W. L. *Inorg. Synth.* **1983**, *22*, 163.

(10) Andreu, P. L.; Cabeza, J. A.; Miguel, D.; Riera, V.; Villa, M. A.; García-Granda, S. *J. Chem. Soc., Dalton Trans.* **1991**, 533.

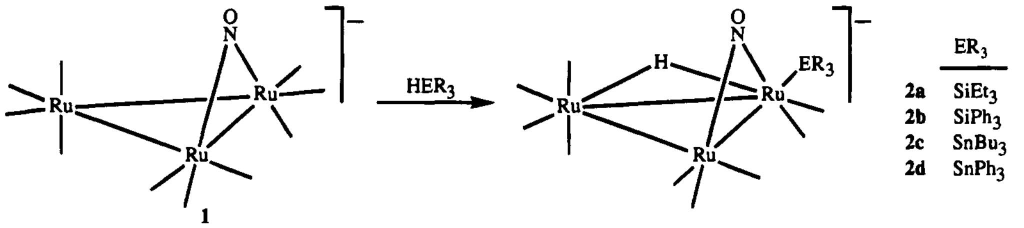
0020-1669/94/1333-5952$04.50/0

Table 1. Selected IR and ^{1}H NMR Data

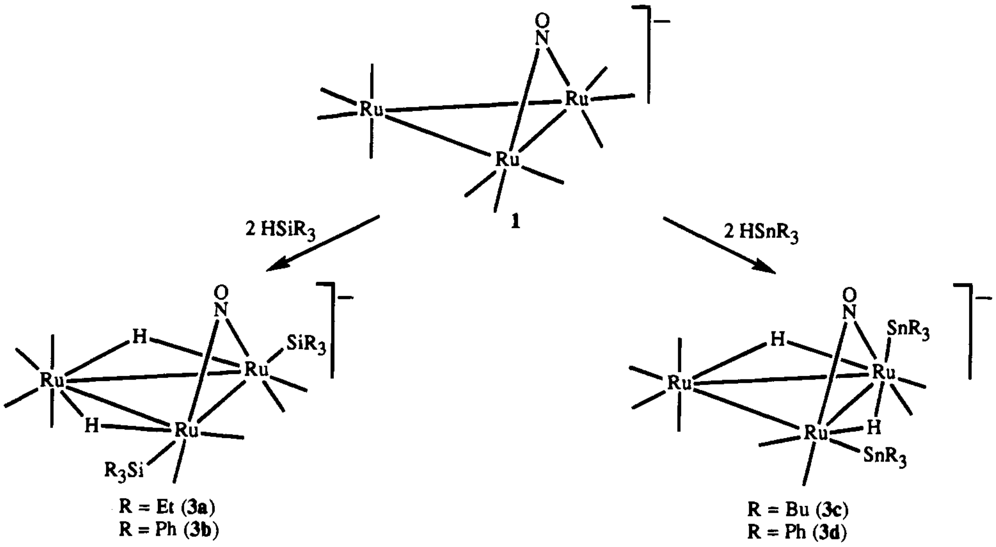
compd	ν(CO)^a/cm^{-1}	δ(μ-H)^b/ppm
2a	2064 (m), 2020 (s), 1989 (s), 1982 (s), 1962 (s), 1940 (m), 1929 (m)	−11.12 (s)
2b	2067 (m), 2026 (s), 1992 (s), 1968 (s), 1943 (m), 1920 (sh)	−11.04 (s)
2c	2065 (m), 2021 (s), 1990 (s), 1980 (s), 1968 (s), 1943 (m), 1926 (m)	−11.40 (s^{c,d})
2d	2070 (m), 2029 (s), 1995 (s), 1980 (s), 1965 (sh), 1948 (m), 1937 (sh)	−11.23 (s^{c,e})
3a	2050 (w), 2036 (m), 2019 (s), 1988 (s), 1960 (s), 1951 (sh), 1932 (sh), 1920 (sh)	−16.84 (s)
3b	2053 (w), 2024 (m), 2017 (sh), 1992 (s), 1967 (s), 1954 (sh), 1924 (sh)	−16.21 (s)
3c	2054 (m), 2014 (s), 1998 (s), 1980 (s), 1959 (s), 1944 (m), 1925 (sh)	−10.27 (s^{c,f}), −13.57 (s^{g,h})
3d	2066 (m), 2029 (sh), 2014 (s), 1992 (s), 1974 (m), 1955 (sh), 1942 (sh), 1923 (sh)	−10.08 (s^{c,i}), −13.63 (s^{g,j})

[a] In THF solution. [b] In CDCl$_3$ solution. [c] With tin satellites. [d] $J(^{119/117}\mathrm{Sn}-^1\mathrm{H}) = 18.3$ Hz. [e] $J(^{119/117}\mathrm{Sn}-^1\mathrm{H}) = 19.1$ Hz. [f] $J(^{119/117}\mathrm{Sn}-^1\mathrm{H}) = 28.6$ Hz. [g] With two pairs of tin satellites. [h] $J(^{119/117}\mathrm{Sn}-^1\mathrm{H}) = 23.4$ and 12.8 Hz. [i] $J(^{119/117}\mathrm{Sn}-^1\mathrm{H}) = 28.9$ Hz. [j] $J(^{119/117}\mathrm{Sn}-^1\mathrm{H}) = 19.2$ and 14.8 Hz.

Scheme 1



Scheme 2



stannane (HER$_3$), in THF solution at reflux (E = Si) or room (E = Sn) temperature, to give the oxidative substitution products [PPN][Ru$_3$(μ-NO)(μ-H)(ER$_3$)(CO)$_9$] (ER$_3$ = SiEt$_3$ (**2a**), SiPh$_3$ (**2b**), SnBu$_3$ (**2c**), SnPh$_3$ (**2d**)). The structure proposed for these complexes in Scheme 1 is supported by their spectroscopic (IR, NMR) and analytical data and also by the structures of the doubly-substituted derivatives **3a-d** (*vide infra*), since **2a-d** have to be intermediates in the synthesis of the latter.

The similarity of the IR spectra of **2a-d** (Table 1) indicates that all these compounds are isostructural. Their ^{1}H NMR spectra show a hydride resonance (Table 1), those of **2c** and **2d** displaying tin satellites with $J(^{119/117}\mathrm{Sn}-^1\mathrm{H})$ coupling constants indicative of a cis arrangement of the hydrido and stannyl ligands.[11] The low temperature (−60 °C) ^{13}C{^{1}H} NMR spectrum of a ^{13}CO-enriched sample of **2d**, taken as a representative example, confirms that the compound contains nine CO ligands (the compound shows CO fluxionality at room temperature). Finally, the cis labilizing effect of the nitrosyl ligand suggests substitution of a CO ligand cis to it.[12,13] Unfortunately, as occurs frequently with other PPN salts of anionic cluster complexes,[4] we could not get crystals to confirm the proposed structure by X-ray diffraction methods.

The reactions of complex **1** with two or more equivalents of tertiary silanes or stannanes gave the disilyl or distannyl derivatives [PPN][Ru$_3$(μ-NO)(μ-H)$_2$(ER$_3$)$_2$(CO)$_8$] (ER$_3$ = SiEt$_3$ (**3a**), SiPh$_3$ (**3b**), SnBu$_3$ (**3c**), SnPh$_3$ (**3d**)).

In this case, the IR spectra of the silyl derivatives **3a** and **3b** are different from those of the stannyl derivatives **3c** and **3d** (Table 1), indicating different structures. In fact, the ^{1}H NMR spectra of **3a** and **3b** only show one hydride resonance, suggesting a symmetric structure, while those of **3c** and **3d** show

---

(11) Cabeza, J. A.; Franco, R. J.; Llamazares, A.; Riera, V.; Bois, C.; Jeannin, Y. *Inorg. Chem.* **1993**, *32*, 4640.

(12) Compound **1** reacts with phosphines and phosphites, at room temperature, to give substituted compounds which contain the *P*-donor ligands in equatorial positions cis to the bridging nitrosyl ligand.[4]

(13) For reactions of silanes and stannanes with triruthenium cluster complexes containing other bridging *N*-donor ligands, see: (a) Cabeza, J. A.; Llamazares, A.; Riera, V.; Triki, S.; Ouahab, L. *Organometallics* **1992**, *11*, 3334. (b) Cabeza, J. A.; García-Granda, S.; Llamazares, A.; Riera, V.; Van der Maelen, J. F. *Organometallics* **1993**, *12*, 157. (c) Cabeza, J. A.; García-Granda, S.; Llamazares, A.; Riera, V.; Van der Maelen, J. F. *Organometallics* **1993**, *12*, 2973. (d) Reference 11.

two hydride resonances, as expected for an asymmetric structure, one with two pairs of tin satellites (indicating the presence of one hydride ligand spanning the Ru−Ru edge which contains both tin atoms) and the other with only one pair of tin satellites (with a $J(^{119/117}Sn-^{1}H)$ indicative of a cis arrangement of the hydrido and stannyl ligands).[11] In order to test whether the observed symmetry of the silyl derivatives **3a** and **3b** could be a consequence of dynamical averaging due to a fluxional process, their ^{1}H NMR spectra were also run at low temperature (−60 °C), but no significant changes were observed, confirming that the hydride ligands do not participate in any dynamical process. The low temperature (−60 °C) $^{13}C\{^{1}H\}$ NMR spectrum of a ^{13}CO-enriched sample of **3c**, taken as a representative example, confirms that the compound contains eight CO ligands (the compound shows CO fluxionality at room temperature). All these spectroscopic data strongly support the structures proposed for these complexes in Scheme 2, but, again, they could not be confirmed by X-ray diffraction studies because the compounds could not be obtained as crystals.

Discussion

The mild conditions required for the reactions of complex **1** with tertiary silanes and stannanes contrast with those required for the reactions of the parent carbonyl $[Ru_3(CO)_{12}]$ with the same reagents,[14,15] which frequently lead to fragmentation of the trimetallic framework giving mono- and binuclear derivatives.[14] The low activation energy of the reactions that lead to **2a-d** has to be related to the cis labilizing effect of the *N*-donor nitrosyl ligand, which facilitates the substitution of carbonyl ligands,[12,13] and to the fact that complex **1** is anionic, being therefore more susceptible to undergo oxidative addition reactions than a neutral or cationic complex.[6]

The isolation of compounds **2a-d**, which contain only 1 equiv of hydrosilane or hydrostannane, contrast with the results reported for the compounds $[PPN][Ru_3(\mu\text{-}H)(\mu\text{-}CO)(CO)_{10}]$[6] and $[Ru_3(\mu\text{-}C_4H_4N_2)(\mu\text{-}CO)_3(CO)_7]$[11] ($C_4H_4N_2$ = pyridazine), which incorporate 2 equiv of hydrosilanes or hydrostannanes regardless of the ratio of the reactants. However, it has been reported that the activated cluster $[Ru_3(CO)_{11}(MeCN)]$ reacts with $HSnPh_3$ at −40 °C to give $[Ru_3(\mu\text{-}H)(SnPh_3)(CO)_{11}]$.[16]

The fact that the disubstituted silyl derivatives (**3a**, **3b**) are symmetric whereas the corresponding stannyl derivatives (**3c**, **3d**) are asymmetric is unprecedented, since, as far as we are aware, there are only two previous examples decribing the incorporation of 2 equiv of tertiary silanes or stannanes to triruthenium clusters and in one case the products are isostructural ($[Ru_3(\mu\text{-}H)(ER_3)_2(CO)_{10}]^-$, E = Si, Sn),[6] whereas in the other ($[Ru_3(\mu\text{-}C_4H_4N_2)(\mu\text{-}H)_2(ER_3)_2(CO)_8]$, E = Si, Sn), the silyl derivatives are asymmmetric while the stannyl derivatives are symmetric.[11]

Unfortunately, the data which could help to rationalize the behavior of hydrosilanes and hydrostannanes in their reactions with carbonyl cluster complexes is still very limited. Therefore, much more work is needed in this area.

Acknowledgment. This work was supported by the DGICYT (Grant PB92-1007). R.J.F. is grateful to MUTIS and to the Instituto de Cooperación Iberoamericana (Madrid, Spain) for postgraduate scholarships.

---

(14) (a) Cotton, J. D.; Knox, S. A. R.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1967**, 965. (b) Cotton, J. D.; Knox, S. A. R.; Stone, F. G. A. *J. Chem. Soc. A* **1968**, 2758. (c) Watkins, S. F. *J. Chem. Soc. A* **1969**, 1552. (d) Knox, S. A. R.; Stone, F. G. A. *J. Chem. Soc. A* **1969**, 2559. (e) Vancea, L.; Graham, W. A. G. *Inorg. Chem.* **1974**, *13*, 511.

(15) Van Buuren, G. N.; Willis, A. C.; Einstein, F. W. B.; Peterson, L. K.; Pomeroy, R. K.; Sutton, D. *Inorg. Chem.* **1981**, *20*, 4361.

(16) Burgess, K.; Guerin, C.; Johnson, B. F. G.; Lewis, J. *J. Organomet. Chem.* **1985**, *295*, C3.