from analysis and spectral features for an $\alpha,\beta$-unsaturated ketone ($^{13}C$ NMR $\delta$ 188.9 (C=O), 140.0 (=C$_\alpha$), 154.7 (=C$_\beta$); IR $\nu_{C=O}$ 1650, $\nu_{C=C}$ 1610 cm$^{-1}$) in a monomeric system (single $^{31}P$ signal at $\delta$ +46.8). The phosphine oxide counterpart of **8** (**6**) also could be made to undergo the internal aldol condensation, but required the presence of a trace of added acid ($p$-toluenesulfonic) catalyst in the refluxing benzene medium. The product (**10**) had mp 97–98 °C and similar spectral features to those of **9**. These bicyclic compounds are members of a new series and may prove to have value as intermediates for construction of multicyclic phosphorus compounds, another area under intense development.[7]

## References and Notes

(1) Supported in part by Public Health Service Grant CA-05507 from the National Cancer Institute.
(2) M. J. Gallagher in "Stereochemistry of Heterocyclic Compounds", Vol. II, W. L. F. Armarego, Ed., Wiley-Interscience, New York, N.Y., 1977, Chapter 5.
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(5) The dienes were prepared by pyrolysis of the *N,N'*-dioxide of the bis(dimethylaminomethyl) derivatives using the procedure of A. C. Cope and E. Ciganek, *Org. Syn.*, **39**, 40 (1959), as a guide. The *trans*-dicarboxylic acids were the source of the amines by the sequence (1) $SOCl_2$, (2) $Me_2NH$, (3) $LiAlH_4$. The commercially available anhydride of *cis*-cyclohexanedicarboxylic acid was converted to the dimethyl ester, epimerized by methanolic sodium methoxide, and hydrolyzed by aqueous KOH to the acid. Cyclobutane and cyclopentanedicarboxylic acids were obtained from diethyl $\alpha,\alpha'$-dibromoadipate and $\alpha,\alpha'$-dibromopimelate, respectively, by cyclization with NaCN, followed by HCl hydrolysis (see R. C. Fuson and T. Y. Kao, *J. Am. Chem. Soc.*, **51**, 1536 (1929); R. C. Fuson and W. Cole, *ibid.*, **60**, 1237 (1938); R. C. Fuson, C. L. Fleming, P. F. Warfield, and D. E. Wolf, *J. Org. Chem.*, **10**, 121 (1945)). The dienes had the expected $^1H$ NMR spectra (P. D. Bartlett, A. S. Wingrove, and R. Owyang, *J. Am. Chem. Soc.*, **90**, 6067 (1968)).
(6) L. D. Quin and R. C. Stocks, *J. Org. Chem.*, **39**, 686 (1974).
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## A Comparison of Allyl and Nitrosyl Coordination in the 18-Electron Complex Allylnitrosylbis(triphenylphosphine)ruthenium and Its CO Adduct

*Sir:*

The dual nature of both allyl and nitrosyl ligands as 1e$^-$ and 3e$^-$ donors in transition metal complexes is well established,[1,2] and recent attention has focused on the catalytic potential which this duality provides.[3-6] Sorely lacking, however, are examples of stable, mixed allyl nitrosyl complexes, and the comparative studies of these ligands and their bonding propensities which such species will allow. To date, only two systems of this type have been reported,[7,8] the most extensively studied being $Fe(NO)(\eta^3\text{-}C_3H_5)L_2$ where L = CO, tertiary phosphine.[8] We wish to report the synthesis and crystal structure of the first platinum group metal complex of this type, and evidence for its reaction with CO to form a five-coordinate species containing a bent nitrosyl.

Reaction of $RuCl(NO)(PPh_3)_2$[9] in benzene or THF with tetraallyltin at room temperature gives the red, air-sensitive $Ru(NO)(\eta^3\text{-}C_3H_5)(PPh_3)_2$, **1**, in 70% yield. Recrystallization from THF/$Et_2O$ affords analytically pure[10] crystals which are stable in air for several weeks. The complex is soluble in $C_6H_6$, THF, and $CH_2Cl_2$, but decomposes rapidly in $CHCl_3$ and $CCl_4$ to form $RuCl_3(NO)(PPh_3)_2$. The IR spectrum of **1** (KBr) shows a nitrosyl stretch at 1620 cm$^{-1}$ (1640 cm$^{-1}$ in $CH_2Cl_2$), while the $^1H$ NMR spectrum exhibits a pattern characteristic of essentially symmetric $\eta^3$-allyl coordination with phosphorus coupling to the anti protons. The $^1H$ NMR spectrum of **1** is shown in Figure 1A and a computer simulation[11] is given in Figure 1B (central proton, $\delta$ 4.70; anti protons, 1.00; syn protons, 2.40 and 2.42 ($^3J_{syn}$ = 4.0 Hz; $^3J_{anti}$ = 10.0 Hz; $J_{PH_{anti}}$ = 6.0 Hz)).

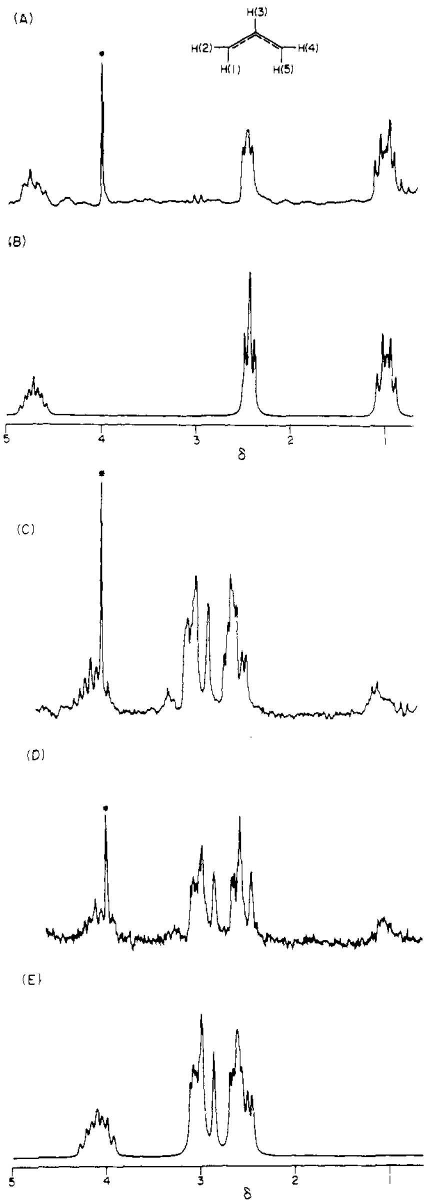


**Figure 1.** $^1H$ NMR spectra of the allyl-nitrosyl complexes in benzene-$d_6$: (A) $Ru(\eta^3\text{-}C_3H_5)(NO)(PPh_3)_2$; (B) computer simulation of spectrum A; (C) $Ru(\eta^3\text{-}C_3H_5)(NO)(CO)(PPh_3)_2$; (D) $^{31}P$-decoupled spectrum of the carbonyl adduct above; (E) computer simulation of spectrum C. Resonances marked with an asterisk (*) are due to traces of $H_2O$ in solvent.

The coordination geometry of **1** and the mode of nitrosyl coordination were unambigously established by a single-crystal x-ray analysis. The complex crystallizes in the monoclinic space group $P2_1$ in a cell of dimensions $a$ = 9.04 (1), $b$ = 17.47 (3), $c$ = 11.51 (1) Å; $\beta$ = 115.39 (5)° with $Z$ = 2. The structure was solved by standard heavy-atom methods and refined by least-squares procedures to final agreement factors $R$ and $R'$ of 0.0299 and 0.0383 for 2074 reflections having $F_O \geqslant 3\sigma(F_O)$ and 159 variables.[12] Tables of final structural parameters and intramolecular distances and angles are available as supplementary material (see paragraph at the end of the paper).

Figure 2 presents a perspective view of the structure of **1**

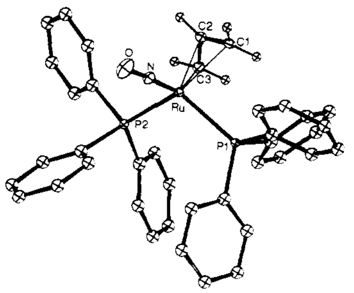


**Figure 2.** A perspective drawing of Ru($\eta^3$-$C_3H_5$)(NO)($PPh_3$)$_2$. Selected bond distances and angles follow: Ru-N, 1.751 (6), N-O, 1.188 (8), $C_1$-$C_2$, 1.38 (1), $C_2$-$C_3$, 1.41 (1), Cl-Ru, 2.214 (6), $C_2$-Ru, 2.130 (8), $C_3$-Ru, 2.258 (8), $P_1$-Ru, 2.391 (4), $P_2$-Ru, 2.344 (3) Å; Ru-N-O, 173.8 (6), P-Ru-P, 104.8 (1), $C_1$-$C_2$-$C_3$, 117.7 (7)°.

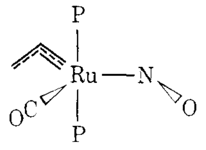
along with important distances and angles. The coordination geometry is found to be a distorted tetrahedron with the nitrosyl group linearly coordinated (Ru-N-O, 173.8 (6)°). As expected, the allyl group is bonded to Ru in trihapto fashion with Ru-C distances of 2.214, 2.130, and 2.258 (8) Å. Thus, both allyl and nitrosyl serve as $3e^-$ donors, and the complex can be viewed as a coordinatively saturated, pseudo-$d^{10}$ system completely analogous to Ru(NO)$_2$($PPh_3$)$_2$[13] and Ru($\eta^3$-$C_3H_5$)$_2$($PPh_3$)$_2$.[14]

The addition of ligands to **1** can be accomplished in one of three ways: (a) conversion of the allyl group from $\eta^3$ to $\eta^1$;[3,8] (b) dissociation of a phosphine[8]; or (c) bending of the metal-nitrosyl moiety. The last pathway, which corresponds to an intramolecular redox reaction[6] and has been discussed in terms of stereochemical control of valence,[2a,15] has not been reported previously for four-coordinate complexes.

Red solutions of **1** in $C_6H_6$, THF, or $CH_2Cl_2$ quickly turn orange in the presence of CO. An IR spectrum of the solution shows the appearance of $\nu_{CO}$ at 1934 cm$^{-1}$ and a slight shift of $\nu_{NO}$ to 1650 cm$^{-1}$. The orange solution is stable under $N_2$, but slowly decomposes (hours) to Ru(CO)$_3$($PPh_3$)$_2$[16] under excess CO, as evidenced by the replacement of the 1934- and 1650-cm$^{-1}$ stretches with a single $\nu_{CO}$ at 1900 cm$^{-1}$. The loss of nitrosyl and allyl ligands by a possible coupling may model a step in the nitric oxide + propylene synthesis of acrylonitrile which uses heterogeneous catalysts.[17] The $^1$H and $^1$H {$^{31}$P} NMR spectra of the orange species (Figures 1C and 1D) indicate an unsymmetrically bonded $\eta^3$-allyl. The chemical shifts of the syn and anti protons are clearly in the region characteristic of $\eta^3$ coordination. (In contrast, $\eta^1$-allyls have typical chemical shifts of $\delta$ 5–6 for terminal protons and 1–3 for the methylene protons.) The complexity of the splitting patterns for 1C and 1D indicates that the allyl is unsymmetrically bonded and that the magnetic nonequivalence of the protons is maintained on the NMR time scale. A computer simulation of the $^1$H NMR spectrum is shown as 1E based on the following assignments: proton 3, $\delta$ 4.08; protons 2 and 4, 2.63 and 3.05; protons 1 and 5, 2.52 and 2.92 ($J_{13}$ = 10.3, $J_{35}$ = 12.2, $J_{23}$ = 6.8, $J_{34}$ = 6.4, $J_{24}$ = 3.4, and $J_{1P}$ = 4.9 Hz). While not unique, the simulation corroborates the assignment of $\eta^3$ bonding. The only significant proton–phosphorus coupling in 1E is between one P and one anti proton.

Through $^{31}$P {$^1$H} NMR,[18] the orange species was established as the bis phosphine complex Ru(NO)(CO)($\eta^3$-$C_3H_5$)($PPh_3$)$_2$, **2.** In benzene solution **1** shows a singlet at +51.3 ppm relative to trimethyl phosphate and a smaller intensity singlet due to $OPPh_3$[19] at +21.8 ppm. Addition of CO leads to replacement of the downfield singlet by a four-line multiplet at +52.0 ppm ($J_{PRuP} \simeq$ 21 Hz) which can only be due to a bis phosphine complex. In addition, two singlets of weak intensity appear at +47.5 ppm and −8.5 ppm corresponding to a monophosphine complex, **3**, and free $PPh_3$, respectively. Addition of free $PPh_3$ causes the +47.5-ppm singlet to decrease in intensity relative to the multiplet. The $^1$H NMR spectrum of **2** is unchanged with added $PPh_3$, but a decrease is noted in the intensity of some initially unassigned resonances at higher field ($\delta$ <2.0) which are due to **3.** Complex **3** is formulated as Ru(NO)(CO)($\eta^3$-$C_3H_5$)($PPh_3$) and the equilibrium between **2** and **3** is in the slow exchange limit at room temperature.

From the spectroscopic evidence obtained, we are able to conclude that **2** is an 18-electron five-coordinate complex with a necessarily bent nitrosyl ligand. The evidence is summarized as follows: (a) from IR spectroscopy **2** is shown to contain both NO and CO ligands; (b) $^{31}$P NMR measurements reveal **2** to be a bis phosphine species; and (c) $^1$H NMR spectroscopy shows the allyl group to have $\eta^3$ coordination, albeit unsymmetrical. Since the addition of CO to **1** increases the electron count by two, and since the allyl coordination remains as $\eta^3$, the nitrosyl ligand must bend to avoid forming a 20-electron species. We thus assign **2** to have the bent nitrosyl structure I in which we assume trans phosphine ligands and a trigonal bipyramidal geometry for an 18-electron species. In this system at least, bending of the nitrosyl is more facile than $\eta^3 \rightarrow \eta^1$ ($\pi \rightarrow \sigma$) conversion of the allyl.[20]



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Further studies probing the $1e^-$–$3e^-$ duality of nitrosyl and allyl in mixed ligand complexes and which utilize this duality in reaction chemistry are underway.

**Acknowledgments.** We thank the National Science Foundation (Grant CHE 76-17440) for support of this research, Matthey Bishop Co., Inc., for a loan of ruthenium salts, Drs. T. Krugh and P. Serpentino for obtaining the $^{31}$P NMR spectra, and Mr. C. Kubiak for help with the structure analysis.

**Supplementary Material Available:** Tables of final structural parameters and intramolecular distances and angles with estimated standard deviations (6 pages). Ordering information is given on any current masthead.

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(9) M. H. B. Stiddard and R. E. Townsend, *Chem. Commun.*, 1372 (1969).
(10) Anal. Calcd for $C_{39}H_{35}NOP_2Ru$: C, 67.20; H, 5.06; N, 2.01; P, 8.89. Found: C, 67.14; H, 5.14; N, 1.98; P, 8.80.
(11) The program used for computer simulations was a version of LAOCN which was incorporated into the EXCHSYS program package by C. B. Powell, Jr., and J. K. Krieger of MIT.
(12) Structural details will be published separately: M. Schoonover, C. P. Kubiak and R. Eisenberg, *in preparation*.
(13) A. P. Gaughan, Jr., B. J. Corden, R. Eisenberg, and J. A. Ibers, *Inorg. Chem.*,

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(17) See, for example, J. M. Kruse, E. I. du Pont de Nemours and Co., U.S. Patent 3 342 847 (Sept 1967). While not explicitly stated, the reaction may proceed through the coupling of nitrosyl and allyl to form 3-nitrosopropene which after tautomeric shifts and dehydration yields the $\alpha,\beta$-unsaturated nitrile.
(18) $^{31}$P NMR spectra were recorded with a JEOL PS-100 FTNMR spectrometer equipped with a JEOL EC-100 computer using a benzene-$d_6$ internal lock. Downfield chemical shifts are reported as positive.
(19) The presence of oxidized phosphine may be due to traces of air which caused partial decomposition of the complex in solution. This resonance was unchanged throughout the course of the experiment.
(20) It should be reiterated that the nitrosyl bonding mode in **2** is not based on a change in $\nu_{NO}$ upon CO coordination. In fact, $\Delta\nu_{NO}$ is not a sensitive probe in systems of this type, and, in some cases, the linear (NO$^+$) to bent (NO$^-$) conversion of coordinated nitrosyl has been accompanied by a slight increase in $\nu_{NO}$ as we observe in the present case. See ref 4 for example in which Rh(NO)L$_3$ ($\nu_{NO}$ 1610 cm$^{-1}$) is observed to form the bent nitrosyl species Rh(NO)I$_2$L$_2$ ($\nu_{NO}$ 1630 cm$^{-1}$).

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# *Additions and Corrections*

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**Photochemical Cycloaddition of Singlet and Triplet Diphenylvinylene Carbonate with Vinyl Ethers** [*J. Am. Chem. Soc.*, **98**, 8438 (1977)]. By FREDERICK D. LEWIS,* RICHARD H. HIRSCH, PAULA M. ROACH, and DOUGLAS E. JOHNSON, Department of Chemistry, Northwestern University, Evanston, Illinois 60201.

Equations 10 and 15 should read as follows:

$$\frac{1}{\Phi_A} = \frac{k_{-e} + k_a + k_{ed}}{k_a} + \frac{k_{-e} + k_a + k_{ed}}{\tau k_a k_e[E]} \qquad (10)$$

$$\frac{1}{\Phi_T} = \frac{(k_a + k_{bd})(k_b + k_{-e} + k_{ed})}{k_a k_b} + \frac{(k_a + k_{bd})(k_b + k_{-e} + k_{ed})}{k_e k_a k_b \tau_T[E]} \qquad (15)$$

The intercept/slope ratio of eq 15 is $k_e\tau_T$, which replaces eq 16. The ordinate of Figure 1 should be labeled $\Phi_A{}^{-1}$ and the numerical values on the ordinate divided by 10.

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**Concerning the Stereochemistry of the S$_N$2′ Reaction in Cyclohexenyl Systems** [*J. Am. Chem. Soc.*, **99**, 3850 (1977)]. By G. STORK* and A. F. KREFT, III, Department of Chemistry, Columbia University, New York, New York 10027.

On p 3850, last paragraph, the statement, "It was however accompanied by the isomer **4** (**2**:**4** = 61:23)" should be followed by . . . "in addition to 10% S$_N$2 and 6% S$_N$1 products".

On p 3851, next to last paragraph, "~60:40 (28% **5**, 12% 6 . . .)" should read "~70:30 (28% **5**, 12% **6**)". In the same paragraph "a syn to anti ratio of 35:65 (17.5% **5**, 32.5% **6**; . . .)" should be "a syn to anti ratio of 35:65 (17.5% **6**, 32.5% **5**)".

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**Concerning the Stereochemistry of the S$_N$2′ Reaction. "Concerted" Allylic Displacement in an Acyclic System: Anti Displacement with Thiolate Anion** [*J. Am. Chem. Soc.*, **99**, 3851 (1977)]. By G. STORK* and A. F. KREFT, III, Department of Chemistry, Columbia University, New York, New York 10027.

Add to footnote 9: "The unlikely possibility that the tetrahydropyranyl ether in ii might have participated as a neighboring group in the sulfide displacement was eliminated by showing that levorotatory 2-methyltetrahydrothiophene is obtained by lithium aluminum hydride reduction of the tosylate of i, followed by cyclic sulfide formation via the dimesylate, as well as by lithium aluminum hydride reduction of the tosylate of iii.

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**Ionization of Carbonyl Compounds in Sulfuric Acid. Correction for Medium Effects by Characteristic Vector Analysis** [*J. Am. Chem. Soc.*, **99**, 4229 (1977)]. By JOHN T. EDWARD* and SIN CHEONG WONG, Department of Chemistry, McGill University, Montreal, Quebec, Canada H3A 2K6.

"2-Hydroxy-2-cyclohexen-1-one" on line 6, first column, p 4231, and Compd (1), Table II, p 4231, should be "3-hydroxy-2-cyclohexen-1-one".

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**Catalysis of Superoxide Dismutation by Iron–Ethylenediaminetetraacetic Acid Complexes. Mechanism of the Reaction and Evidence for the Direct Formation of an Iron(III)–Ethylenediaminetetraacetic Acid Peroxo Complex from the Reaction of Superoxide with Iron(II)–Ethylenediaminetetraacetic Acid** [*J. Am. Chem. Soc.*, **99**, 5220 (1977)]. By GREGORY J. MCCLUNE, JAMES A. FEE,* GARY A. MCCLUSKY, and JOHN T. GROVES,* Biophysics Research Division and Department of Biological Chemistry, and Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109.

Author Gary A. McClusky's name was mispelled. There should be no "e" in the name.

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**Kinetics and Mechanism of the Alkyl and Aryl Elimination from $\eta^5$-Cyclopentadienylalkyl(and -aryl)dicarbonyliron(II) Complexes Initiated by Mercury(II) Halides** [*J. Am. Chem. Soc.*, **99**, 5295 (1977)]. By LOUIS J. DIZIKES and ANDREW WOJCICKI,* McPherson Chemical Laboratory, The Ohio State University, Columbus, Ohio 43210.

The caption for Figure 2 (p 5301) should end in: ". . . with HgCl$_2$ in isopropyl alcohol at 25 °C".

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**"Hydrophobic Interaction" and Solvation Energies: Discrepancies between Theory and Experimental Data** [*J. Am. Chem. Soc.*, **99**, 5408 (1977)]. By RICHARD D. CRAMER III, Smith Kline & French Laboratories, Philadelphia, Pennsylvania 19101.

In Table I, the entries in the last column for Kr, Xe, and CF$_4$ should read 34.52, 42.21, and 45.37, respectively. However, all the correlations and conclusions reported are unchanged, being based on the correct molecular volume values".

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**Disproportionation of Saturated Alkali Metal Ketyls to Give Enolates and Alcoholates: a General Reaction That Has Been**