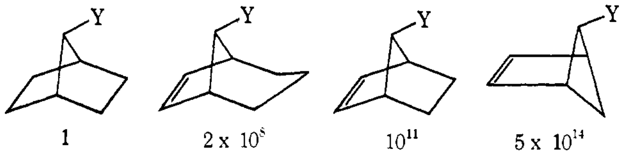
Table II. Rate Ratios (Unsaturated/Saturated) of Related Cyclopentene Systems

Compounds	k_{unsat}/k_{sat}	Ref
I, II	10^{11}	1
Vc, X-OTs	1.9×10^5	This work and ref 10
III, IV	0.25	4

oping positive charge are extremely crucial in the overall effect of anchimeric assistance of the carbon–carbon double bond in the cyclopentenyl system.[12]

Acknowledgment. This work was supported in part by a grant from the Petroleum Research Fund, administered by the American Chemical Society.

[12] The recent report of the solvolysis of a derivative of the *exo*-bicyclo[2.1.1]hex-2-en-5-yl system (S. Masamune, S. Takada, N. Nakatsuka, R. Vukov, and E. N. Cain, *J. Amer. Chem. Soc.*, **91**, 4322 (1969)) allows a comparison of the relative rates of the three related cyclopentenyl systems with the norbornyl system at 25°.



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Oxidative Additions and Catalysis of Olefin Hydrogenation by Tris(triphenylphosphine)nitrosylrhodium

Sir:

Organotransition metal chemistry is conveniently organized into patterns of analogous reactions such as oxidative additions whereby d^n complexes add two-electron oxidants forming d^{n-2} products.[1] At least a few examples of oxidative additions are known for each even d^n configuration, but d^8 [2] and more recently d^{10} complexes[3] have been the most thoroughly studied.

The present work stems from our interest in expanding the scope of d^{10} oxidative additions to neutral complexes of elements to the left of the nickel triad by exploring reactions of nitrosyls. This project led us to consider another question which ultimately may be more significant.

The nitrosyl ligand usually acts as NO^+ bonding linearly and forming analogs to carbonyl compounds one triad to the right.[4] However, the bonding and geometries of other nitrosyl complexes are controversial. Recent X-ray diffraction studies have revealed examples where the M-N-O angle approaches 120°[5] and the ligand may be considered as NO^-, whereas other complexes exhibit intermediate angles.[6] It seems likely that the two extreme forms may not represent deep energy minima, but that a wide range of angles may be accessible, perhaps giving rise to fluxional behavior. Inasmuch as the limiting forms, NO^+ and NO^-, are usually found in complexes whose coordination geometries reflect the implied oxidation state of the central metal, a conformational deformation of the other ligands about the metal might be expected to accompany any wide amplitude bending of the NO group. The most important result of such a deformation would be the creation of a vacant coordination site at the central metal reflecting the implied increase in its oxidation state. Inasmuch as coordinative unsaturation is a key feature of many homogeneous metal catalysts, a thermally accessible or chemically induced conformational change of this type could confer on a nitrosyl complex catalytic activity not found with its carbonyl cognate.

This hypothesis remains speculative, but in those few cases in which the reactions of nitrosyl complexes have been compared with carbonyl analogs, striking differences are found. Examples include mechanisms of ligand replacement reactions[7] and catalysis of diene dimerization.[8] Catalysis of olefin hydrogenation by the rhodium nitrosyl **1a** described below can be added to this list.

The rhodium and iridium nitrosyls, **1a** and **1b**, were prepared by bubbling NO through a boiling THF solution of the appropriate trichloride in the presence of excess Ph_3P and granulated zinc, affording yields of 98 and 40%.[9]

$$MX_3 \cdot 3H_2O + 3L \xrightarrow[\text{THF, 65°}]{\text{Zn, NO}} M(NO)L_3$$

$$L = Ph_3P \qquad \mathbf{1a},\ M = Rh; \quad \mathbf{b},\ M = Ir$$

Both nitrosyls undergo a series of oxidative addition reactions with reagents such as halogens, mercuric halides, hydrogen halides, alkyl halides, and acyl halides. Roper[10] has recently reported reactions of the iridium complex **1b**, but certain of his results are different from those for the rhodium complex **1a** described herein.

Treatment of **1a** with I_2 or HgI_2 afforded the five-coordinate diiodide **2**

$$Rh(NO)L_3 + I_2 \longrightarrow \underset{\mathbf{2}}{Rh(NO)I_2L_2} + L$$

elemental mercury being formed in the latter case. The NO band shifts from 1610 to 1630 cm^{-1} during the reactions (Table I) in contrast to Roper's[10] result with the iridium complex where the product has a lower (1560 cm^{-1}) NO band. A phosphine ligand is ejected during these reactions.

Benzoyl chloride adds to **1a** forming a five-coordinate benzoyl adduct **3a**,

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[1] J. P. Collman, *Accounts Chem. Res.*, **1**, 136 (1968).

[2] J. P. Collman and W. R. Roper, *Advan. Organometal. Chem.*, **7**, 54 (1968).

[3] (a) R. Ugo, *Coord. Chem. Rev.*, **3**, 319 (1968); (b) J. P. Birk, J. Halpern, and A. L. Pickard, *Inorg. Chem.*, **7**, 2672 (1968); *J. Am. Chem. Soc.*, **90**, 4491 (1968).

[4] (a) W. P. Griffith, *Advan. Organometal. Chem.*, **7**, 211 (1968); (b) B. F. G. Johnson and J. A. McCleverty, *Progr. Inorg. Chem.*, **7**, 277 (1966).

[5] D. J. Hodgson, N. C. Payne, J. A. McGinnety, R. G. Pearson, and J. A. Ibers, *J. Am. Chem. Soc.*, **90**, 4486 (1968).

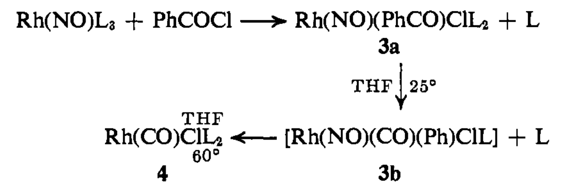
[6] A. T. McPhail and G. A. Sim, *J. Chem. Soc., A*, 1858 (1968), and references therein.

[7] D. E. Morris and F. Basolo, *J. Am. Chem. Soc.*, **90**, 2531 (1968), and references therein.

[8] J. P. Candlin and W. H. James, *J. Chem. Soc., C*, 1856 (1968).

[9] The rhodium complex was also prepared by the earlier method: W. Hieber and K. Heinecke, *Z. Anorg. Allgem. Chem.*, **316**, 321 (1962).

[10] C. A. Reed and W. R. Roper, *Chem. Commun.*, 155 (1969).



$$\begin{tikzcd}
 & \mathrm{Rh(NO)L_3 + PhCOCl} \arrow[r] & \underset{\mathbf{3a}}{\mathrm{Rh(NO)(PhCO)ClL_2 + L}} \arrow[d, "\mathrm{THF}"', "25^\circ"] \\
 & \underset{\mathbf{4}}{\mathrm{Rh(CO)ClL_2}} & \underset{\mathbf{3b}}{\mathrm{[Rh(NO)(CO)(Ph)ClL] + L}} \arrow[l, "\mathrm{THF}", "60^\circ"']
\end{tikzcd}$$

After 8 days in THF, **3a** is converted into a poorly characterized brown crystalline complex, **3b**, whose ir spectrum shows the absence of a benzoyl group and the presence of a carbonyl and a nitrosyl group (Table I). Heating the benzoyl adduct in THF affords the known rhodium carbonyl **4**, probably by way of **3b**. The fate of the other products has not been determined.

Table I. Infrared Spectra

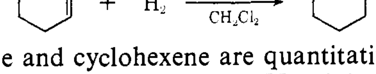
Compound	γ_{NO}(KBr), cm^{-1}	Misc
$Rh(NO)L_3$ (**1a**)	1610	
$Ir(NO)L_3$ (**1b**)	1600	
$Rh(NO)I_2L_2$ (**2**)	1628	
$Rh(NO)PhCO)ClL_2$ (**3a**)	1608	1660, 860 (PhCO)
$Rh(NO)(CO)(Ph)ClL$ (**3b**)	1630	1970 (CO), 338 (Rh-Cl)
$Rh(NOH)Cl_3L_2$ (**5a**)		3330, 3230 (OH?) 2470, 2380 (OD?)
$Rh(HNO)Cl_3L_2$ (**5b**)	1638	3280, 3230 (NH?) 2460, 2380 (ND?)

Dry HCl reacts with **1a** to form a mixture of two apparently tautomeric adducts **5a** and **5b**. Three equivalents of HCl is consumed and H_2 is evolved, but in low (9%) yield (vacuum line and vpc analysis).

$$\mathrm{Rh(NO)L_3 + 3HCl} \longrightarrow \underset{\mathbf{5a}}{\mathrm{Rh(NOH)Cl_3L_2}} + \underset{\mathbf{5b}}{\mathrm{Rh(HNO)Cl_3L_2}}$$

The less soluble yellow adduct **5a**, which occluded solvents and proved difficult to purify, was transformed into the orange isomer **5b** by treatment with methanol. The dichloride, $RhCl_2(NO)L_2$, does not react with HCl under these conditions, even though Roper found $IrCl_2(NO)L_2$ to be the product of HCl addition to **1b**. The ir spectra of **5a** and **5b** support our supposition that these may be tautomeric complexes of the unknown nitroxyl. Both exhibit NH or OH bands (Table I) which are appropriately shifted when DCl is used. The yellow isomer **5a** lacks a band attributable to an NO group, but **5b** exhibits an NO band at 1635 cm^{-1}.

The rhodium nitrosyl **1a** does not form a stable adduct with H_2 as judged from the constancy of its uv-visible and ir spectra under a H_2 atmosphere. Nevertheless, **1a** effectively catalyzes the hydrogenation of terminal and cyclic olefins.



1-Hexene and cyclohexene are quantitatively reduced in CH_2Cl_2 solutions at 25° and 55 psi (or 1 atm). If peroxide-free olefins are used in an O_2-free environment, olefin isomerism does not take place and the catalyst can be recovered unchanged. Triphenylphosphine retards these hydrogenations. It is perhaps significant that a formally d^{10} complex activates hydrogen. Under the same conditions, the iridium analog **1b** fails to catalyze these reactions; however, in benzene at 85° **1b** does catalyze the reduction of 1-hexene with isomerization.

Treatment of cyclohexene with D_2 in the presence of **1a** afforded $C_6H_{10}D_2$ in >99% isotopic purity (mass spectral analysis), suggesting that this catalyst will prove to be stereospecific. Only one other compound,[11] RhL_3Cl, is reported to catalyze deuteration without H, D scrambling. Further studies on the use of **1a** in catalysis and the mechanism of these reactions are continuing.

Acknowledgment. The authors are grateful to the National Science Foundation (Grant GP 9101) and the Center for Materials Research at Stanford University for support which made this research possible.

[11] J. A. Osborn, F. H. Jardine, and G. Wilkinson, *J. Chem. Soc.*, *A*, 1711 (1968).

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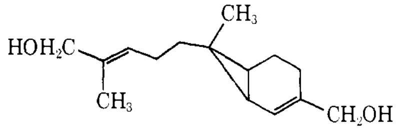
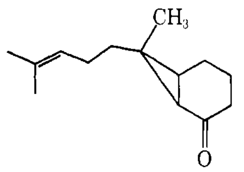
The Total Synthesis of *dl*-Sirenin

Sir:

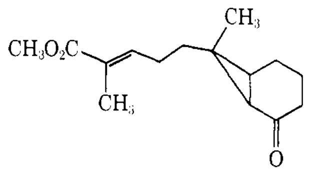
The structure I has recently been established for sirenin, the sperm attractant produced by the female gametes of the water mold, *Allomyces.*[1-4] We were drawn to the problem of synthesizing it because it appeared that the intramolecular addition of olefinic diazo ketones which was introduced some years ago[5] should be a particularly suitable method for the stereospecific construction of the sirenin molecule, *e.g.*, *via* II. Furthermore, the unsaturated acid needed as a precursor of II (*cf.* VI, R = OH) could obviously be made easily by procedures which we had developed in another connection.[6]



I



II



III

Treatment of geranyl chloride (in ether–HMPA) with excess allylmagnesium bromide in ether by the general method previously described[6] produced the triene

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[1] L. Machlis, *Physiol. Plant.*, **11**, 181 (1958).

[2] L. Machlis, W. H. Nutting, M. W. Williams, and H. Rapoport, *Biochemistry*, **5**, 2147 (1966).

[3] L. Machlis, W. H. Nutting, and H. Rapoport, *J. Amer. Chem. Soc.*, **90**, 1674 (1968).

[4] W. H. Nutting, H. Rapoport, and L. Machlis, *ibid.*, **90**, 6434 (1968).

[5] G. Stork and J. Ficini, *ibid.*, 83, 4678 (1961). This method is especially useful in the construction of II because of the stereospecific nature of ketocarbene additions; *cf.* G. Stork and M. Gregson, *ibid.*, **91**, 2373 (1969), footnote 6.

[6] G. Stork, P. A. Grieco, and M. Gregson, *Tetrahedron Lett.*, 1393 (1969). The geranyl chloride, bp 64–65° (0.5 mm) (incorrectly reported as 64–65° (0.05 mm) by Stork), was made from pure geraniol obtained from geraniol "Palma Rosa" through the courtesy of International Flavors and Fragrances.