

Registry No. 1, 99249-28-2; 2a, 99249-29-3; 2b, 99295-87-1; 3, 99249-30-6; 4a, 99249-31-7; 4b, 99295-88-2; 5, 99249-32-8; 5 (3-ene), 99249-33-9; 6a, 99249-34-0; 6b, 99295-89-3; 7, 99249-35-1; 8a, 99249-36-2; 8b, 99295-90-6; 9, 99249-37-3; 10a, 99249-38-4; 10b, 99295-91-7; 11, 99249-39-5; 12a, 99249-40-8; 12b, 99295-92-8; 13, 99249-41-9; 14a, 99249-42-0; 14b, 99249-43-1; 15, 99249-44-2; 16a, 99249-45-3; 16b, 99295-93-9; $\text{MeO}\overline{\text{C}}=\text{CH}(\text{CH}_2)_3\text{CHBr}$, 1728-36-5; $(\text{PhCH}_2\text{OCH}_2\text{CHOH})_2$, 17401-06-8; $\overline{\text{C}}\text{H}=\text{CH}(\text{CH}_2)_2\text{CO}$, 930-30-3; $\overline{\text{C}}\text{H}=\text{CH}(\text{CH}_2)_3\text{CO}$, 1121-66-0; $\text{MeBrC}(\text{CH}_2)_4\text{CO}$, 10409-47-9; $\text{TsO}-\overline{\text{C}}\text{H}(\text{CH}_2)_2\text{COCH}_2\text{CH}_2$, 23511-04-8; $\text{AcC}=\text{CHCH}_2(\text{CH}_2)_2\text{CH}_2$, 932-66-1; $\text{HOCH}_2\text{CH}=\text{CMeCH}_3$, 556-82-1; $\text{OHCCH}=\text{CMeCH}_3$, 107-86-8; (*E*)- $\text{HOCH}_2\text{CH}=\text{CH}(\text{CH}_2)_3\text{CO}_2\text{Me}$, 76871-77-7; (*E*)- $\text{HOCH}_2\text{CH}=\text{CH}(\text{CH}_2)_3\text{CHO}$, 99249-48-6; 2-bromocyclohexane ketal, 99267-50-2; 2-bromo-2-methylcyclohexanone ketal, 99249-46-4; 4-tosylcyclohexanone ketal, 99249-47-

Supplementary Material Available: Experimental details for the preparation of compounds 1-16, infrared, proton magnetic resonance, and mass spectral data for compounds 1-16, and carbon magnetic resonance spectral data for compounds 2, 4, 6, 8, 10, 12, 14, and 16 (15 pages). Ordering information is given on any current masthead page.

Pyrazolyl-Bridged Iridium Dimers. 10.¹ Sequential Addition at the Metal Centers in a Diridium Configuration. Oxidatively Induced Relocation of a Bent, Terminal Nitrosyl Group To Occupy a Bridging Site

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Development of the chemistry of metal nitrosyl complexes has lagged behind that of the transition-metal carbonyl family despite certain obvious similarities between the character of nitrogen monoxide (nitric oxide, NO) and carbon monoxide as ligands.² The unique significance of CO as an accessible C₁ feedstock has provoked research into all aspects of its coordination behavior,² while the ambivalent electronic character of the NO ligand has worked against efforts to classify its properties.³ Recently, however, interest in catalytic activation of NO (reductively⁴ in combustion emissions, to N₂O or N₂, or C-N bond formation, via oximes⁵ or to⁶ diamines, or for⁷ oxygen-transfer to organic substrates) has led to a more systematic search for parallels with existing steps in metal carbonyl chemistry. Thus migratory insertion^{8,9} of coordinated NO and alkene⁶ and alkyne¹⁰ insertion

Table I. IR^a and ¹H NMR^b Data

compd	$\nu_{\text{NO}}/\text{cm}^{-1}$	¹ H NMR/ppm		
2	1680	7.67 d ^c (2),	7.57 d ^c (2),	6.49 t ^d (2)
3	1700 ^e	7.71 d ^c (2),	7.50 d ^c (2),	6.50 t ^d (2)
4a	1630	7.75 d ^c (4),	6.40 t ^d (2)	

^a KBr pellet. ^b Recorded at 250.0 MHz, Bruker WM250 Spectrometer, CD₂Cl₂ solution; relative intensities are given in parentheses. ^c H³/H⁵ of μ -pz. ^d H⁴ of μ -pz. ^e ν_{CO} at 2065 cm⁻¹.

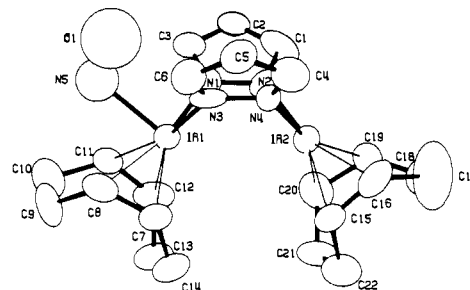


Figure 1. ORTEP drawing of the cation in complex 2. Selected bond distances and angles: Ir(1)-Ir(2), 3.224 (1); Ir(1)-N(1), 2.021 (19); Ir(1)-N(3), 2.051 (19); Ir(1)-N(5), 2.081 (33); N(5)-O(1), 1.012 (50); Ir(2)-N(2), 2.041 (21); Ir(2)-N(4), 2.077 (17); Ir(1)-C(7), 2.209 (25); Ir(1)-C(8), 2.262 (24); Ir(1)-C(11), 2.255 (25); Ir(1)-C(12), 2.211 (24); Ir(2)-C(15), 2.143 (24); Ir(2)-C(16), 2.166 (27); Ir(2)-C(19), 2.173 (24); Ir(2)-C(20), 2.122 (28) Å. N(1)-Ir(1)-N(3), 89.4 (8)^o; N(2)-Ir(2)-N(4), 87.9 (7)^o; Ir(1)-N(5)O(1), 111.3 (41)^o. Unresolved disorder or high thermal motion results in the uncertainties in the positions of N(5) and O(1); See also: Mingos, D. M. P.; Ibers, J. A. *Inorg. Chem.* 1971, 10, 1035. Mingos, D. M. P.; Robinson, W. T.; Ibers, J. A. *Ibid.* 1971, 10, 1043.

into metal(μ -NO) bonds, as well as protonation and alkylation of terminal¹¹ and μ_3 -bridging¹² NO groups, are now established. We describe two-center oxidative-addition to a cationic diridium(II) complex as a result of which a bent, terminal NO group takes up a bridging position. Such a process has not been reported previously, although the analogous transformation involving CO is well-known² and like isoelectronic carbonyl complexes [Cr(η -C₅H₅)(NO)₂]₂ is subject to intramolecular terminal/bridge ligand site exchange.¹³

Addition to a solution in CH₂Cl₂ of the purple-red diridium(I) complex [Ir(COD)(μ -pz)]₂ (1, COD = cycloocta-1,5-diene; pzH = pyrazole) of NOBF₄ resulted in immediate darkening of the reaction mixture. Stirring (1 h) then filtration, precipitation with Et₂O and finally recrystallization from CH₂Cl₂/Et₂O afforded lustrous, purple-black crystals of a product (2) which was deduced to be a cationic diridium nitrosyl complex on the basis of IR, NMR (Table I), and analytical data.¹⁴ The geometry of the cation, which was determined using single-crystal X-ray diffraction,¹⁵ is shown in Figure 1. Treatment of compound 2 with

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(14) Compound 2. Anal. Calcd for C₂₂H₃₀BF₄Ir₂N₅O: C, 31.02; H, 3.55; N, 8.22. Found: C, 30.95; H, 3.31; N, 8.01. Compound 3. Anal. Calcd for C₂₃H₃₀BF₄Ir₂N₅O₂: C, 31.40; H, 3.44; N, 7.96. Found: C, 31.32; H, 3.40; N, 8.53. Compound 4a. Anal. Calcd for C₂₂H₃₀BCl₂F₄Ir₂N₅O: C, 28.64; H, 3.28; N, 7.59. Found: C, 28.31; H, 3.67; N, 7.40. Compound 4b. Anal. Calcd for C₂₂H₃₀BF₄Ir₂N₅O: C, 23.90; H, 2.74; N, 6.33. Found: C, 24.25; H, 2.79; N, 5.85.

(15) Crystal data for compound 2: *M*, 851.7; monoclinic; space group P2₁/n; *a* = 14.645 (5) Å, *b* = 13.446 (4) Å, *c* = 13.391 (2) Å; β = 112.24 (2)^o; *V* = 2441 Å³; *Z* = 4; *D*_{calcd} = 2.32 g cm⁻³; Picker four circle diffractometer, Mo K α (λ = 0.71069 Å) radiation, μ = 105.4 cm⁻¹; 2852 observed reflections refined to a conventional *R* = 0.070 (*R*_w = 0.071).

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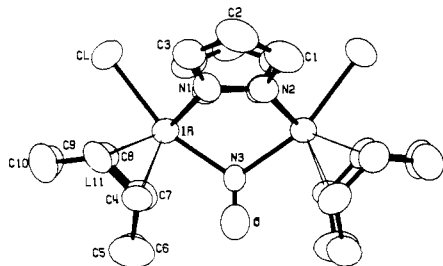


Figure 2. ORTEP drawing of the cation in complex **4a**. Selected bond distances and angles: Ir–Ir, 3.428 (1); Ir–Cl, 2.395 (3); Ir–N(1), 2.067 (9); Ir–N(3), 2.096 (9); Ir–C(4), 2.303 (12); Ir–C(7), 2.286 (12); Ir–C(8), 2.264 (13); Ir–C(11), 2.283 (14) Å. N(1)–Ir–Cl, 84.1 (3)⁰; N(3)–Ir–Cl, 162.0 (4)⁰; N(3)–Ir–N(1), 83.3 (4)⁰; Ir–N(3)–Ir, 109.7 (7)⁰; O–N(3)–Ir, 125.2 (3)⁰.

CO gas (1 atm, CH₂Cl₂ solvent) afforded a purple adduct formulated¹⁴ as the carbonyl complex [Ir₂(COD)₂(μ-pz)₂(NO)(CO)]BF₄ (**3**). Bubbling HCl gas through a solution in CH₂Cl₂ of compound **2** led to isolation of a brick-red product **4a** which was characterized by X-ray methods as the tetrafluoroborate salt of a nitrosyl-bridged diiridium(III) cation,¹⁶ the geometry of which is depicted in Figure 2. Treatment of the cation **2** with I₂ yielded (ca. 45%) the diiodo analogue **4b** of **4a**, and the same complex was obtained almost quantitatively via NO⁺ oxidation (NOBF₄) of cation **2** resulted in conversion to the orange dimethylidiriidium(II) complex¹⁷ **6**.

The structure of the cation in complex **2** is striking in that the observed Ir–Ir distance of 3.224 (1) Å is actually marginally longer than that (3.216 Å) in the d⁸–d⁸ dimer **1**, suggesting that the former should be regarded as a d⁸–d⁶ species [i.e., oxidation at only one metal center, to Ir(III)]. By contrast two-center oxidation of **1** and related compounds (which may be accompanied by Ir₂ bond formation) leads to formation of adducts for which a d⁷–d⁷ diiridium(II) formalism is appropriate.^{17–19} Interaction between the adjacent Ir centers in the cation **2** may be opposed by the very strong trans influence associated with nonlinear MNO coordination:³ the Ir(1)–N–O linkage is severely bent (although uncertainty in the bond angle is high due to disorder, see Figure 1), consistent with electron-rich character for Ir(1). There is, however, no evidence for localized mixed-valence (d⁸–d⁶) character in equatorial bond distances which are equal to each Ir center. The bridged cation in compound **4a** is constrained to regularity by twofold crystallographic symmetry along the NO vector with Ir₂ separation of 3.428 (1) Å as expected¹⁹ for two nonbonded Ir(III) centers linked by three bridging ligands.

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Supplementary Material Available: Fractional atomic coordinates and temperature parameters, anisotropic temperature parameters, and tables of bond distances and angles and observed and calculated structure factors for cations **2** and **4a** (27 pages). Ordering information is given on any current masthead page.

(16) Crystal data for compound **4a** (bis(dichloromethane) solvate): *M*_r = 1092.5; orthorhombic; space group *Ibca*; *a* = 15.027 (4) Å, *b* = 13.658 (4) Å, *c* = 32.033 (9) Å; *V* = 6574 Å³; *Z* = 8; *D*_{calc} = 2.21 g cm⁻³; Picker four circle diffractometer Mo Kα (λ = 0.71069 Å) radiation, μ = 83.1 cm⁻¹; 1860 observed reflections refined to a conventional *R* = 0.042 (*R*_w = 0.045).

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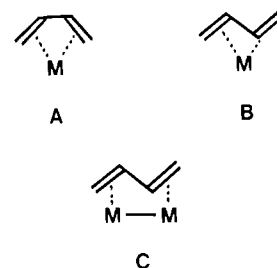
New Mode of Ligation for 1,3-Butadiene to Two Metal Centers. Synthesis and Structure of [(*i*-Pr)₂PCH₂CH₂CH₂P(*i*-Pr)₂]Rh]₂(μ-η³-η³-C₄H₆): A Partial Butadiene Sandwich

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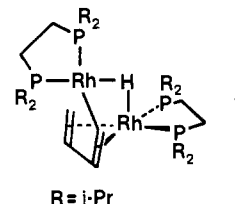
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1,3-Butadiene, the simplest acyclic conjugated diene, normally binds to mononuclear transition-metal centers in the η⁴-*cis* mode³ A, as found in (η⁴-C₄H₆)Fe(CO)₃, for example. More recently,



the less stable η⁴-*trans* form B has been observed⁴ in metallocene derivatives of the formula (η⁴-C₄H₆)M(η⁵-C₅H₅)₂ (M = Zr, Hf). When two or more metal centers are proximate, as in polynuclear metal clusters, the *s*-*trans* bridging mode C has been characterized,⁵ as found in (μ-η²-η²-C₄H₆)Os₃(CO)₁₀. In this paper, we detail a completely new type of ligating mode for 1,3-butadiene with two metal centers, wherein each metal interacts in a trihapto (η³) fashion with a partially "sandwiched" *cis*-1,3-butadiene fragment.

A previous report⁶ from this laboratory outlined the high yield synthesis of **1** from 1,3-butadiene and the corresponding binuclear



rhodium hydride [(*i*-Pr)₂PCH₂CH₂P(*i*-Pr)₂]Rh]₂(μ-H)₂ (**2a**). This transformation established that certain binuclear rhodium hydrides could deviate from reaction pathways normally associated with mononuclear systems. To examine the effect of chelate ring size on this reaction, we allowed 1,3-butadiene to react with [(*i*-Pr)₂PCH₂CH₂CH₂P(*i*-Pr)₂]Rh]₂(μ-H)₂ (**2b**);⁷ this latter binuclear hydride contains the bidentate phosphine 1,3-bis(diisopropylphosphino)propane⁸ (dipp), which generates a six-membered

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