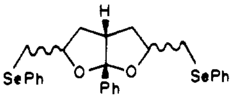
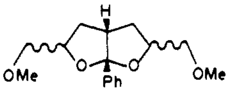
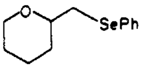
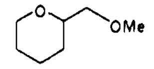
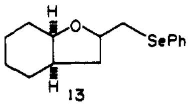
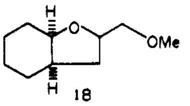
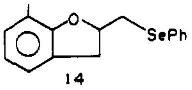
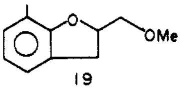
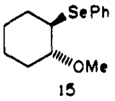
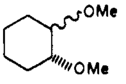
Table I. Physical Constants Evaluated for Photoinduced Single Electron Transfer from Organoselenium Compounds (**5–8**)

substrate	product[a,b] compositn in MeOH (%)	ϕ_{dissap}[c]	ϕ_{lim}[d]	K_{qET}[e] ($\times 10^{10}$ M^{-1} S^{-1})	K_{qET}[f] ($\times 10^{10}$ M^{-1} S^{-1})	$E_{1/2}$(ox)[g] (ev)	ΔG_{ET}[h]
5	PhSeSePh[i]	0.012	0.05	1.92 ± 0.005	1.59	1.35	−18.90
6	PhCH$_2$OMe (73) PhCH$_2$CH$_2$Ph (5) (PhCH$_2$Se)$_2$ (18) Se metal	0.021	0.12	0.54 ± 0.005	0.54	1.60	−13.08
7	n-C$_4$H$_9$OMe (76.4) (n-C$_4$H$_9$Se)$_2$ (23.2)	0.015	0.14	0.47 ± 0.004	0.59	1.65	−11.99
8	n-C$_8$H$_{17}$OMe (61.4) PhSeSePh (38.3)	0.020	0.17	0.44 ± 0.004	0.26	1.62	−12.66

[a] Characterized by identical GC (column: OV-17, 10%) retention time compared with authentic sample and GC mass (column: methyl silicone capillary). [b] The products mentioned are the primary photoproducts, confirmed by irradiating for shorter periods, and the numbers in parentheses are relative GC yields. [c] Light intensity was evaluated by uranyl oxalate actinometry. [d] At infinite donor concentration measured from a plot of ϕ^{-1} vs $[Q]^{-1}$. [e] From fluorescence quenching Stern–Volmer plot. [f] From reciprocal plot of ϕ^{-1} vs $[Q]^{-1}$. [g] Referred to saturated calomel electrode (SCE), using tetraethylammonium perchlorate ass supporting electrolyte, in dry acetonitrile (CH$_3$CN). [h] ΔG_{ET} is expressed in kcal/mol; reductive half-wave potential for DCN ($E_{1/2}$(red) = −1.28 eV) and $E_{0,0}$ = 3.45 eV values were used and taken as such from Mattes and Farid: Mattes, S. L.; Farid, S. *Organic Photochemistry*; Padwa, A., Ed.; Marcel Decker Inc.: New York, 1983; Vol. 6, p 233. [i] The cationic part of the cleavage reaction product (C$_2$H$_5$OMe) could not be isolated, possibly due to low boiling point.

Table II. Deselenenylation of Organoselenium Substrates

Entry	Substrates	Products[a]	Yield[b] (%)
1	 11	 16	70
2	 12	 17	80
3	 13	 18	78
4	 14	 19	70
5	 15	 20	60[c]

[a] Characterized by ^{1}H NMR and mass spectrometry. [b] Isolated yields, but not optimized. [c] Stereochemistry not confirmed.

methanol resulted in a high yield of deselenenylated product (**16–20**) with no side products (Table II).

At this point we reasoned, due to our previous observation[1] and present success, that direct irradiation of a mixture of alken-1-ol (**21** and **22**) and PhSeSePh[16] in the presence of **2** might lead to a one-pot sequential selenenylation and deselenenylation reaction. To this end, we irradiated a mixture of **21** (10 mM), **1** (5 mM), and **2** (1 mM) in methanol for 30 h, which gave **17** in 70% yield as the major product[17,18] (Scheme II). A control experiment of **21** and **22** without **1** does not show any observable product, which is also supported from the insignificant fluorescence quenching of ^{1}DCN*. These results are coherent with the literature reports[19] that only electron-rich olefins undergo electron-transfer processes with cyanoarenes. The most significant achievement of this finding has been the quantitative recovery of both PhSeSePh (97%) and DCN (98%) after the reaction. Further mechanistic and synthetic aspects of this reaction are in progress.

Acknowledgment. B.B.V.S.S. thanks the CSIR for financial assistance.

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(16) PhSeSePh does not absorb any light under the present experimental conditions.

(17) 12 as the primary photoproduct was confirmed from the partial photolysis of **21** for 8 h: ^{1}H NMR (CDCl$_3$, 300 MHz) 7.45 (m, 2 H), 7.20 (m, 3 H), 3.94 (m, 1 H) 3.42 (m, 2 H), 3.01 (dd, 1 H, J = 7.2 and 12.2 Hz), 2.90 (dd, 1 H, J = 7.2 and 12.4 Hz), and 1.2–1.82 (m, 6 H); m/e^+ 256, 172, 157, 85. This substantiates the sequential nature of the reaction.

(18) GC analysis of the crude reaction mixture also showed one small peak (<10–12%) which could be the methanol addition product of episelenonium cation.

(19) (a) Mally, J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 825. (b) Footnote *h* given in Table I.

Preparation and Electronic Characterization of M$_2$(CCR)$_4$(PMe$_3$)$_4$: A Class of Conjugated Transition-Metal Complexes

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Received March 5, 1990

Conjugated organic molecules and polymers comprise an extensive and fundamentally important class of molecules for which there is not a comparably developed and well-defined counterpart in transition-metal chemistry.[1] The dearth of such metal-containing analogues is surprising in view of the fact that their logical building blocks, namely, complexes that contain multiple metal–ligand[2] or metal–metal[3] bonds, are known in abundance and are well-characterized structurally and electronically. Our interest in conjugated metal complexes was motivated by the belief that the incorporation of multiply bonded transition-metal centers into the backbone of an unsaturated organic chain should, given the widely tunable optical properties of metal complexes and the relative ease with which they support open-shell electronic configurations, significantly enhance the diverse physical properties possessed by conjugated organic molecules; dyes,[4] conducting polymers,[5,6] and carbon-based nonlinear optical materials[6,7] are

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[‡] NSF Presidential Young Investigator (1987–1992); Camille and Henry Dreyfus New Faculty Awardee (1987–1992).

(1) Molecular and electronic structural analogies between metal complexes and conjugated organic molecules are discussed in the following: Wheeler, R. A.; Hoffmann, R.; Strähle, J. *J. Am. Chem. Soc.* **1986**, *108*, 5381–5387.

(2) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley: New York, 1988.

(3) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Wiley: New York, 1982.

(4) Zollinger, H. *Color Chemistry*; VCH: New York, 1987.

(5) Skotheim, T. A., Ed. *Handbook of Conducting Polymers*; Marcel Dekker: New York, 1986.

(6) Prasad, P. N., Ulrich, D. R., Eds. *Nonlinear Optical and Electroactive Polymers*; Plenum: New York, 1988.

(7) (a) Hann, R. A., Bloor, D., Eds. *Organic Materials for Nonlinear Optics*; Royal Society of Chemistry: London, 1989. (b) Chemla, D. S., Zyss, J., Eds. *Nonlinear Optical Properties of Organic Molecules and Crystals*; Academic Press: Orlando, 1987.

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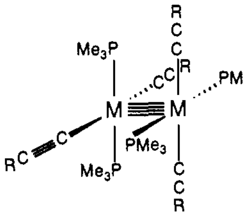
Table I. $^1(\delta \rightarrow \delta^*)$ Transition Energy and Intensity Data for $M_2X_4(PMe_3)_4$ Complexes

M	X	$\bar{\nu}_{max}$, cm^{-1}	ϵ_{max}, $M^{-1}\ cm^{-1}$	ref
Mo	Cl	17 090	3110	12c
Mo	Me	16 920	*a*	*b*
Mo	Br	16 720	4060	12c
Mo	NCO	16 210	8050	12d
Mo	I	15 720	5250	12c
Mo	NCS	14 930	6680	12d
Mo	$CCCMe_3$ (**1**)	14 770	5600	*b*
Mo	$CCSiMe_3$ (**2**)	14 450	5970	*b*
Mo	$CCCHMe_2$ (**3**)	14 770	*a*	*b*
Mo	CCPh (**4**)	13 390	9240	*b*
W	Cl	15 150	4170	12c
W	$CCCMe_3$ (**5**)	12 810	6870	*b*

[a] Not measured. [b] This work.

but a few examples of such species. Herein we report the preparation and characterization of a series of alkynyl-substituted, quadruply metal–metal bonded complexes of the type $M_2(CCR)_4(PMe_3)_4$ that are conjugated in a $\pi(CC)$–$\delta(MM)$–$\pi(CC)$ sense and which may be viewed as a class of metallapolyynes.

Addition of 4 equiv of LiCCR to a 0 °C solution of $M_2Cl_4(PMe_3)_4$ (M = Mo,[8] W[9]) in dimethoxyethane results in the formation of a complex mixture of products from which a compound can be isolated in 35–80% yield whose elemental analysis and NMR spectroscopic data[10] are consistent with the formulation $M_2(CCR)_4(PMe_3)_4$ (M = Mo, R = CMe_3 (**1**), $SiMe_3$ (**2**), $CHMe_2$ (**3**), Ph (**4**); M = W, R = CMe_3 (**5**)). While we have not been able to completely structurally characterize these species via X-ray crystallography due to disorder problems with the four derivatives that we have examined to date, the X-ray data indicate[11] that they possess the same point symmetry (D_{2d})[8,12] as the other members of the $M_2X_4(PMe_3)_4$ class. Consistent with this, the ^1H, ^{13}C, and ^{31}P NMR data establish that there is only a single type each of alkynyl and trimethylphosphine ligand in each complex; the chemical shifts of the ^{13}C resonances assigned to the alkynyl α- and β-carbon atoms are consistent with an η^1 coordination mode for this ligand,[13] while the appearance of the ^1H and ^{13}C resonances of the trimethylphosphine ligands as virtually coupled triplets is indicative of a trans phosphine ligand arrangement about each metal center. That the metal–metal distances of these complexes are typical of those of the $M_2X_4(PMe_3)_4$ class may be inferred from the similarity of the metal–metal stretching frequency observed for **2** (362 cm^{-1})[14] to those found for crystallographically characterized $Mo_2X_4(PMe_3)_4$ derivatives (X = Cl, Br, I: $\nu_1(Mo_2)$ = 343–355 cm^{-1}, $r(Mo_2)$ = 2.125–2.130 Å).[12c]



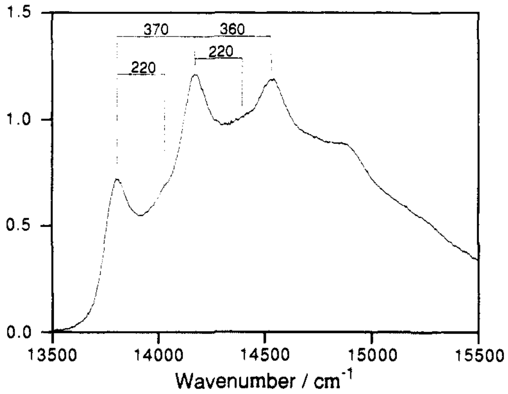


Figure 1. Electronic absorption spectrum of $Mo_2(CCSiMe_3)_4(PMe_3)_4$ in 2-methylpentane at 77 K. Spacings (cm^{-1}) of the two major vibronic progressions are indicated.

The electronic and resonance Raman spectra of the $M_2(CCR)_4(PMe_3)_4$ complexes manifest an unprecedented degree of ligand orbital mixing with the formally metal–metal-localized δ and δ^* frontier orbitals, by comparison to other members of the $M_2X_4(PMe_3)_4$ class. Specifically, the $^1(\delta \rightarrow \delta^*)$ transition, the energy and intensity of which have been noted to be sensitive to such mixing,[15] is observed to lie at considerably lower energy for $M_2(CCR)_4(PMe_3)_4$ than for $M_2X_4(PMe_3)_4$ derivatives with simple ligands (Table I). Noteworthy among the alkynyl complexes are the lower energy and much higher intensity observed for the R = Ph complex compared to those seen for complexes that possess saturated R groups. Both the red shift of these $^1(\delta \rightarrow \delta^*)$ transitions relative to those of halide-containing complexes and the R-group dependence of the transition energy and intensity are substantially larger than would be anticipated on the basis of the charge-transfer-mixing mechanism that has been used to interpret the ligand-induced spectral shifts of other quadruply bonded dimers.[15b] More direct evidence for strong M_2 and CCR orbital mixing is provided by the vibrational fine structure that is resolved in the $^1(\delta \rightarrow \delta^*)$ band. In contrast to the vibronic structure displayed by other $M_2X_4(PMe_3)_4$ complexes at 77 K, which consists of a dominant progression in $\nu(M_2)$ (the excited-state frequency of which is ca. 10% lower than the ground-state value) that maximizes at the 0–2 vibronic transition,[16] the spectrum of **2** (Figure 1) reaches a maximum after *one* quantum of a mode whose frequency is slightly *greater* than the ground-state metal–metal stretch. Given the metal–metal bonding–antibonding nature of the $^1(\delta \rightarrow \delta^*)$ transition, this frequency appears to be more consistent with the assignment of the progression to $\nu(MoC)$ (ground-state $\nu(MoC)$ = 397 cm^{-1})[14] than to $\nu(Mo_2)$.[17] That an unusually large excited-state distortion indeed occurs along this coordinate is borne out by the resonance Raman spectrum of **2** obtained upon $^1(\delta \rightarrow \delta^*)$ excitation, which displays the $\nu_1(Mo_2)$ and $\nu_2(MoC)$ fundamentals with an intensity ratio of 2.3:1. By comparison, the ν_1/ν_2 intensity ratios reported for other quadruply bonded complexes are typically 20–30:1,[12c,18] consistent with their $\nu(M_2)$-dominated vibronic spectra.

We believe that the low energy, R-group dependence, and unusual vibronic profile of the $^1(\delta \rightarrow \delta^*)$ transitions of these species and the marked resonance enhancement of the $\nu_2(MC)$ Raman mode reflect significant frontier orbital mixing between the $[\delta,\delta^*]$ orbitals of the M_2 core and the $[\pi,\pi^*]$ orbitals of the CCR ligands. Such conjugation is possible because the metal–metal δ and δ^* orbitals are of π symmetry with respect to the equatorial ligands.[19]

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(8) Cotton, F. A.; Extine, M. W.; Felthouse, T. R.; Kolthammer, B. W. S.; Lay, D. G. *J. Am. Chem. Soc.* **1981**, *103*, 4040–4045.

(9) Schrock, R. R.; Sturgeoff, L. G.; Sharp, P. R. *Inorg. Chem.* **1983**, *22*, 2801–2806.

(10) See supplementary material.

(11) Schaefer, W. P.; Stoner, T. C.; Hopkins, M. D., unpublished results for **3**.

(12) (a) Girolami, G. S.; Mainz, V. V.; Andersen, R. A.; Vollmer, S. H.; Day, V. W. *J. Am. Chem. Soc.* **1981**, *103*, 3953–3955. (b) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Tatz, R. J. *J. Am. Chem. Soc.* **1984**, *106*, 1153–1154. (c) Hopkins, M. D.; Schaefer, W. P.; Bronikowski, M. J.; Woodruff, W. H.; Miskowski, V. M.; Dallinger, R. F.; Gray, H. B. *J. Am. Chem. Soc.* **1987**, *109*, 408–416. (d) Cotton, F. A.; Matusz, M. *Inorg. Chem.* **1988**, *27*, 2127–2131.

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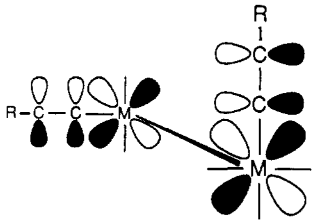
(14) Resonance Raman data for **2** (THF solution, λ_{ex} 648.7 nm): $\nu_3(MoP)$ 254 cm^{-1} (intensity = 10), $\nu_1(Mo_2)$ 362 (100), $\nu_2(MoC)$ 397 (44), $2\nu_1$ 722 (13), $(\nu_1 + \nu_2)$ 758 (11), $2\nu_2$ 795 (7).

(15) (a) Manning, M. C.; Trogler, W. C. *J. Am. Chem. Soc.* **1983**, *105*, 5311–5320. (b) Hopkins, M. D.; Gray, H. B.; Miskowski, V. M. *Polyhedron* **1987**, *6*, 705–714.

(16) Hopkins, M. D.; Gray, H. B. *J. Am. Chem. Soc.* **1984**, *106*, 2468–2469.

(17) A weak 220-cm^{-1} progression, possibly attributable to $\nu(MoP)$, is also observed.

(18) (a) Clark, R. J. H.; Stead, M. J. *Inorg. Chem.* **1983**, *22*, 1214–1220. (b) Clark, R. J. H.; D'Urso, N. R. *J. Am. Chem. Soc.* **1978**, *100*, 3088–3091.



These findings suggest to us that compounds of this type that possess differentially substituted electron-donating and -withdrawing R groups should behave as push-pull metallapolyynes and that low-dimensional conjugated chains of metal dimers may be prepared from μ-η^1:η^1-diynyl ligands;[20] we are currently investigating these materials and are examining additional manifestations of conjugation in the physical properties of the complexes reported herein.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for the support of this research.

Supplementary Material Available: A listing of NMR spectroscopic data and elemental analyses for compounds **1–5** (1 page). Ordering information is given on any current masthead page.

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(19) The CCR π (and π^*) orbitals that lie perpendicular to the metal–metal bond transform as $a_2 + b_1 + e$ and hence can mix with the $b_1\delta$ and $a_2\delta^*$ orbitals. Stronger mixings (on energetic grounds) should occur among the CCR [π,π^*] orbitals that lie parallel to the M_2 axis ($a_1 + b_2 + e$) and the metal–metal e[π,π^*] orbitals, but we cannot judge their magnitude since we lack experimental probes of these orbitals.

(20) Dicarboxylato-bridged quadruply bonded tetranuclear complexes have recently been reported for which there is electrochemical evidence for electronic coupling: Cayton, R. H.; Chisholm, M. H. *J. Am. Chem. Soc.* **1989**, *111*, 8921–8923.

An Unprecedented Propellane-to-Spirofused Skeletal Rearrangement Upon Oxidative Demetalation of CpCo-Complexed Polycyclic Dienes: Synthesis of a Pentacyclic, Potential Precursor to Strychnine

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Received January 2, 1990

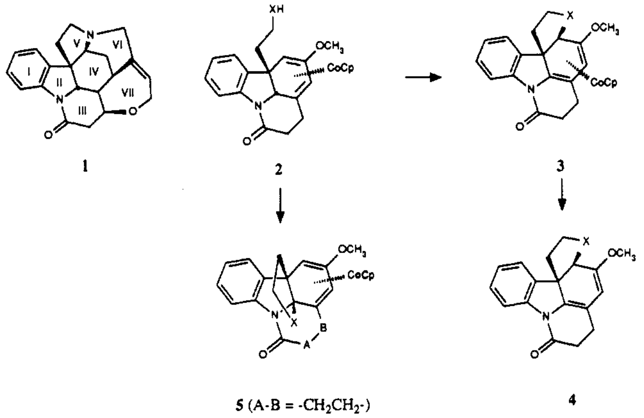
The presence of what might be envisaged to become rings I–IV of the synthetically challenging, convulsant poison strychnine (**1**)[1] in complexes of the type **2**, recently made readily available by the CpCo-mediated one-step fusion of rings III and IV to the indole nucleus,[2] led us to initiate investigations aimed at effecting the oxidative cyclization of **2** to **3**, in analogy to related ring-closures found with (diene)$Fe(CO)_3$ complexes.[3] In contrast to the chemistry of the latter, we report that compounds **2** undergo non-demetalative oxidation to the propellanes **5**, *from which the ligands can be removed intact or in the spirofused form* **4** (containing, according to IUPAC, a "non-free spiro union"), *depending upon the reaction conditions.*

Table I. Oxidative Cyclizations of Substrates 2

substrate 2[a]	conditions[b]	yields of products,[c] % 5	6	7	ratio of 5:6:7[d]
a (X = O)	A	96 (61)			
	B	93			15:1:1
	C	9	(17)	(34)	2:3:6
b (X = NH)	A	(67)		(7)	8:0:1
c (X = $NC(O)CH_3$)	A[e]				1:0:2
d (X = $NCH_2C_6H_5$)	A	93 (64)			25:1:<1
	B	84			
	D	(79)			≥20:0:0
e (X = $NCH_2CH{=}CH_2$)	A	95			25:1:0
f (X = $NCH_2C{\equiv}CH$)	A	(34)			≥10:1:0

[a] Prepared from the complexes in ref 2 by protodesilylation [$(CH_3)_3N^+CH_2C_6H_5F^-$, 1–1.2 equiv, DMSO or THF–DMSO (1:1), 80–110 °C, 1–17 h, 79–94%], followed by standard functional group manipulations of X. [b] A, aged MnO_2; B, Aldrich "activated" MnO_2; C, γ-MnO_2 (all three reagents 20–30 molar equiv); D, $Cp_2Fe^+PF_6^-$, $[(CH_3)_2CH)]_2NCH_2CH_3$. Reactions were performed in CH_2Cl_2, at 23 °C, for 5–30 min, except in the case of **2c**. [c] Yield of crude material; that of analytically pure material in parentheses. For **5f**, the yield applies to the overall conversion of **2a** (see footnote *a*). [d] By ^1H NMR of the crude reaction mixture. A zero entry means that signals for that product could not be detected. [e] In boiling solvent, 16 h.

The results of the first step are summarized in Table I[4] and merit the following comments. (1) Oxidation of model complex **2a** by the moderately active MnO_2,[5] particularly when aged, produces propellane **5a** in high yields, contaminated with small amounts of **6a** and **7a**.[6] Use of the more active γ-MnO_2[5] (all in excess) favors side-chain dehydrogenation (**7a**), as well as demetalation (**6a**), whereas $BaMnO_4$[7] affords a mixture of products (qualitative ^1H NMR experiment) in which **5a** and **6a** predominate. (2) Primary amine **2b** furnishes a relatively large proportion of overoxidized **7b**, the generation of which can be suppressed by alkylation of the nitrogen (substrates **2d–f**); acylation (**2c**), on the other hand, has the opposite effect, while at the same time reducing the rate of cyclization dramatically. Significantly (vide infra), the cleanest transformation is caused by ferricenium ion {$Cp_2Fe^+PF_6^-$, 2 equiv; $[(CH_3)_2CH]_2NCH_2CH_3$, 2 equiv; CH_2Cl_2, 25 °C, 10 min; **2d** → **5d**, 79%}. (3) One notes that conversion of **2** to **5** requires loss of the dienylic hydrogen located exo with respect to the CpCo fragment, in contrast to an $Fe(CO)_3$ system.[3a] (4) That the metal fragment is crucial to the success



5 (A-B = $-CH_2CH_2-$)
6 (free diene ligand from **5**)
7 (A-B = $-CH{=}CH-$)

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