Diethyl ether adducts of bis(pentamethylcyclopentadienyl)europium(II) and -ytterbium(II). Excited-state energy transfer with organolanthanoid complexes

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pentadienyl ring possessing a twofold rotational disorder. The geometry of the $Co_3(NO)_2$ core in **2**, which has C_1—1 site symmetry, is essentially the same as that of **1**, as shown from a bond-length comparison—viz., the independent Co–Co distance of 2.399 (3) Å in **1** vs. three Co–Co distances of range 2.395 (1)–2.414 (1) Å (mean, 2.403 Å) in **2** and the independent Co–NO distance of 1.843 (9) Å in **1** vs. six Co–NO distances of range 1.856 (4)–1.873 (4) Å (mean, 1.863 Å) in **2**. The mean Co–Co bond lengths in **1** and **2** are significantly longer than that of 2.370 (1) Å in the 46-electron $Co_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CO)_2$[8] but are virtually identical with those in other sterically uncrowded, 48-electron bicapped tricobalt clusters with either carbon- or nitrogen-attached atoms (of similar size)—e.g., the $[Co_3(\eta^6\text{-}C_6H_6)_3(\mu_3\text{-}CO)_2]^+$ monocation (2.399 Å)[17] as the $[BPh_4]^-$ salt, $Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}CO)(\mu_3\text{-}NC(O)NH_2)$ (2.400 Å),[9] and the $[Co_3(\eta^5\text{-}C_5H_4Me)(\mu_3\text{-}NO)(\mu_3\text{-}NH)]^+$ monocation (2.406 Å)[9] as the $[BPh_4]^-$ salt. The Co–NO bond lengths in **1** and **2** are comparable to those in the 48-electron $[Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)]^+$ monocation (mean 1.869 Å)[9] but are considerably smaller than the corresponding Co–CO bond lengths in the 46-electron $Co_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CO)_2$ (1.951 (6) Å)[8] and in the 48-electron $Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}CO)(\mu_3\text{-}NC(O)NH_2)$ (mean, 1.930 Å).[9] The shorter Co–NO bond lengths are likely due to the greater electron π-acceptor ability of the triply bridging nitrosyl ligand (relative to a triply bridging carbonyl ligand) in these clusters.

Cyclic voltammetric measurements[18] (Figure 2) revealed that **1** and **2** have similar reversible redox behavior with each CV displaying a one-electron oxidation couple to the 47-electron monocation and a one-electron reduction couple to the 49-electron monoanion. The designation of each redox couple as a one-electron process is based upon the equivalent peak current heights of the oxidation and reduction couples in **1** and in **2** together with an equimolar mixture of **2** and $[Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)]^+[BPh_4]^-$ (which was independently shown[9] to have a reversible one-electron reduction couple) exhibiting equivalent peak current heights for the two reduction couples. A comparative analysis of the corresponding $E_{1/2}$ values between **1** and **2** shows that **2** is easier to oxidize (by 0.10 V) but more difficult to reduce (by 0.09 V) than **1**; this trend is consistent with the enhanced electron donating ability of the C_5H_4Me ligands (relative to the C_5H_5 ligands) which gives rise to increased electron density at the cobalt atoms and hence to higher energies for both the HOMO (from which one electron is removed upon oxidation) and LUMO (to which one electron is added upon reduction).

Work in our laboratories is currently directed at the following: (1) isolation of the oxidized 47-electron and reduced 49-electron species of **1** and **2** for spectroscopic and structural characterization to determine the redox-generated changes in geometry; and (2) protonation and alkylation reactions of the neutral parents (**1** and **2**) involving possible N–O bond-cleavage transformations.

Acknowledgment. This research was supported by the National Science Foundation. We are especially grateful to Dr. R. B. Cody (Nicolet Analytical Instruments) for obtaining a mass spectrum of **1** with a Nicolet FT-MS 1000 mass spectrometer. Special thanks are also due to Dr. Robert L. Bedard for helpful suggestions in carrying out the electrochemical measurements.

Registry No. **1**, 58071-54-8; **2**, 98689-82-8; $Fe_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}NO)_2$, 52124-51-3; $Co(\eta^5\text{-}C_5H_5)(CO)_2$, 12078-25-0; $Fe_2Co(\eta^5\text{-}C_5H_5)_3(CO)(NO)_2$, 98689-81-7; $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$, 12194-69-3; $Fe_2(\eta^5\text{-}C_5H_5(\mu\text{-}CO)_2(CO)_2$, 12154-95-9; $Co_2(\eta^5\text{-}C_5H_4Me)_2(\mu\text{-}NO)_2$, 85454-64-4.

Supplementary Material Available: Six tables listing the atomic parameters, intramolecular distances and bond angles, and the observed and calculated structure factor amplitudes for both $Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}NO)_2$ (**1**) and $Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}NO)_2$ (**2**) (33 pages). Ordering information is given on any current masthead page.

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(17) Olson, W. L.; Dahl, L. F., submitted for publication.

(18) Cyclic voltammetric data were obtained with a BAS-100 Electrochemical Analyzer with the electrochemical cell enclosed in a N_2-filled Vacuum Atmospheres drybox. The working electrode was a platinum disk; the reference electrode was a vicor-tipped, aqueous SCE separated from the test solution by a vicor-tipped salt bridge filled with a 0.1 M $TBAPF_6/CH_3CN$ solution. The counterelectrode was a platinum coil. Solution volumes were about 5 mL of CH_2Cl_2 with an approximate concentration of 10^{-3} M of cluster compound.

Diethyl Ether Adducts of Bis(pentamethylcyclopentadienyl)europium(II) and -ytterbium(II): Excited-State Energy Transfer with Organolanthanoid Complexes

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Summary: The title compound $(\eta^5\text{-}Me_5C_5)_2Eu^{II}\cdot OEt_2$, **1**, exhibits photoluminescence (uncorrected $\lambda_{max} \approx 730$ nm) at 295 K in toluene solution; a radiative quantum yield of ~0.04 and lifetime of ~400 ns were measured for **1** under these conditions. Quenching of the emission from **1** by $(\eta^5\text{-}Me_5C_5)_2Yb^{II}\cdot OEt_2$, **2**, in toluene solution demonstrates energy transfer between two organolanthanoid complexes. A Stern–Volmer treatment of the quenching of the emission intensity and lifetime of **1** yields a bimolecular quenching rate constant of $\sim 7 \times 10^8$ M^{-1} s^{-1}.

Recent studies of organolanthanoid complexes have demonstrated that photoluminescence can be observed at 295 K from a variety of Yb(III),[1] Tb(III),[2] and Yb(II),[3,4] adducts possessing cyclopentadienyl ligands or derivatives thereof. We report in this communication that a Eu(II) organolanthanoid complex, $(\eta^5\text{-}Me_5C_5)_2Eu^{II}\cdot OEt_2$, **1**, emits at room temperature. Moreover, photoluminescence from **1** can be quenched in toluene solution by energy transfer to $(\eta^5\text{-}Me_5C_5)_2Yb^{II}\cdot OEt_2$, **2**. To our knowledge, this is the first example of excited-state energy transfer involving two organolanthanoid complexes.

Compound **1**[5] is a red-brown solid which yields bright red photoluminescence at 295 K when excited with visible or near-UV light. Toluene solutions of **1** are reddish brown

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(1) Schlesener, C. J.; Ellis, A. B. *Organometallics* **1983**, *2*, 529.

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(4) Thomas, A. C.; Ellis, A. B. *J. Lumin.* **1984**, *31/32*, 564.

(5) Tilley, T. D. Ph.D. Thesis, University of California at Berkeley, 1982. Private communication from R. A. Andersen. Samples of **2** were prepared as described from YbI_2 and $Na(Me_5C_5)$ in Et_2O. Anal. Calcd. for $C_{24}H_{40}OYb$ (**2**): Yb, 33.43. Found: Yb, 32.6, 33.4. Samples of **1** were prepared by a variation of this procedure using $EuBr_2$. Anal. Calcd for $C_{24}H_{40}OEu$ (**1**): C, 58.05; H, 8.12; Eu, 30.60. Found: C, 57.81; H, 7.98; Eu, 30.3. Analyses for C and H were obtained from Analytische Laboratorien, Engelskirchen, West Germany; metal analyses were performed by wet ashing the organolanthanoid complex with H_2SO_4/HNO_3, followed by EDTA titration with hexamethylenetetramine buffer and xylenol orange indicator.

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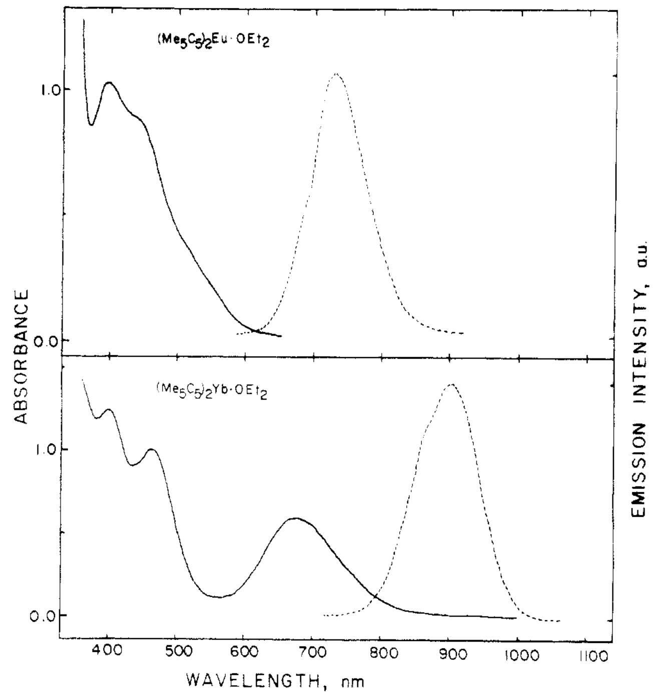

Figure 1. Absorption (solid lines) and photoluminescence (dashed lines) spectra of 1 (top panel) and 2 (bottom panel) in toluene solution at 295 K. The concentrations of 1 and 2 were 1.7 and 2.6 mM, respectively. Photoluminescence spectra were excited at 457.9 nm.

and exhibit an electronic band at 400 nm ($\epsilon \approx 590$ M^{-1} cm^{-1}) with a shoulder at 450 nm; when excited with visible or near-UV light, these solutions emit in the red with an uncorrected band maximum at 730 nm. Figure 1 presents these spectral features. Other significant photoluminescence properties of 1 are its radiative quantum efficiency ϕ_r of ~0.04 and its lifetime τ of 400 ± 40 ns at 295 K.[6] These values yield a unimolecular rate constant for radiative decay of ~1 × 10^5 s^{-1}. This value and the breadth (fwhm ≈ 1700 cm^{-1}) of the photoluminescence band are typical of the interconfigurational $4f^65d \rightarrow 4f^7$ transitions observed for Eu^{2+} in a variety of environments; however, the band maximum is remarkably red-shifted relative to the blue photoluminescence commonly observed for Eu^{2+} doped into glasses and crystals and for Eu^{2+} complexes with cryptands.[7] Also noteworthy is a shoulder at ~700 nm in the photoluminescence spectrum of 1. The emissive lifetime is constant throughout the photoluminescence band at 295 K. This property, in conjunction with the invariance of the spectrum with photoluminescence quenching and in ether solution (vide infra), suggests that there are multiple excited states of 1 contributing to its photoluminescence spectrum which are in thermal equilibrium. Also consistent with this notion is the disappearance of the high-energy shoulder upon cooling a Nujol mull of 1 to 12 K.

The photoluminescence properties of 1 afford a means for probing bimolecular excited-state processes, although the compound's substantial ground-state reactivity precludes the use of many common acceptors. A Yb(II) species, 2,[5] offers a means for exploring energy transfer: 1 and 2 are both strong reducing agents with a common Lewis base and, as shown in Figure 1, 2 has a low-lying excited state, characterized by an absorption band at 670 nm and photoluminescence with an uncorrected band maximum at 900 nm. Assignments for the bands of 2 are currently under investigation.

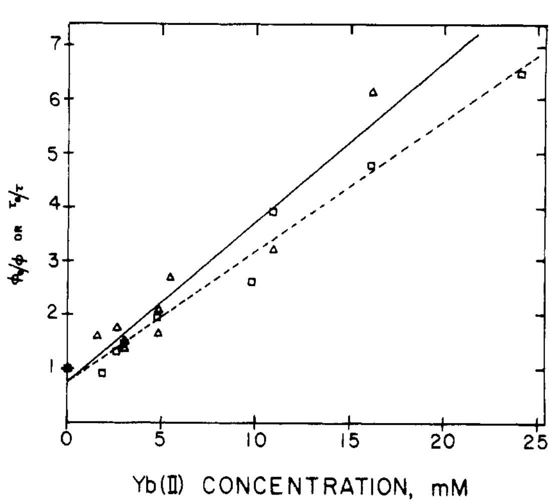

Figure 2. Stern–Volmer plots of photoluminescence quenching (ϕ_0/ϕ; □) and lifetime (τ_0/τ; △) data with corresponding dashed and straight lines of best fits. The points presented were obtained with 570-nm excitation using either a filtered Xe lamp or an Ar$^+$-pumped dye laser and are a composite of three separate experiments; for each experiment, the photoluminescence lifetime and intensity were measured for each aliquot of quencher added. The concentration of 1 in these experiments is ~5 mM.

When 2 is added to toluene solutions of 1, the absorption spectrum is a simple superposition of the two constituent spectra. Furthermore, the photoluminescence spectrum of 1 is quenched uniformly and the photoluminescence lifetime is shortened. Figure 2 presents Stern–Volmer plots of the observed quenching using 570-nm excitation.[8] Although slightly different slopes are obtained for the two sets of quenching data, they are the same within experimental error, the compounds being extremely air- and moisture-sensitive. Using an average slope of 270 M^{-1} and the lifetime of 400 ns in the absence of 2, a bimolecular rate constant for energy transfer of ~7 × 10^8 M^{-1} s^{-1} is obtained.

A potential complication to this analysis is the lability of lanthanoid adducts.[1] Conceivably, loss of the Lewis base from 1 could occur in competition with energy transfer. To investigate this possibility, we repeated these experiments in diethyl ether solution where adduct dissociation should be minimized. In this solvent, there is virtually no change in the absorption and photoluminescence spectra of either 1 or 2 compared to toluene solution.[9] Moreover, similar quenching obtains, yielding a rate constant for energy transfer of ~8 × 10^8 M^{-1} s^{-1}.

In summary, energy transfer between two organolanthanoid complexes has been demonstrated to occur with a rate constant of nearly 10^9 M^{-1} s^{-1}. This value is near the diffusion-controlled limit and demonstrates that energy transfer between two organolanthanoid complexes can be rapid.

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(6) Radiative quantum yields were obtained as described in: Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991 with 402- and 500-nm excitation using cresyl violet perchlorate as a standard (φ_r of 0.55: Magde, D.; Brannon, J. H.; Cremers, T. L.; Olmsted III, J. *J. Phys. Chem.* **1979**, *83*, 696); since part of the sample photoluminescence lies to the red of the standard's emission, the ϕ_r value should be treated as only an estimate. Lifetimes were obtained with 402-nm excitation as described in: Olken, M. M.; Biagioni, R. N.; Ellis, A. B. *Inorg. Chem.* **1983**, *22*, 4128 except that a Molectron UV-12 nitrogen laser/DL-10 dye laser served as the excitation source.

(7) Sabbatini, N.; Ciano, M.; Dellonte, S.; Bonazzi, A.; Bolletta, F.; Balzani, V. *J. Phys. Chem.* **1984**, *88*, 1534 and references therein.

(8) These experiments were conducted in a 1.0-mm path length cell using a front-surface geometry. This arrangement minimizes the absorption of exciting and emitted light by 2; the photoluminescence intensity data in Figure 2 are uncorrected for these effects.

(9) The uncorrected photoluminescence band maximum of 2 blue-shifts in diethyl ether by ~20 nm to 880 nm.

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Registry No. 1, 84254-55-7; 2, 74282-47-6; Na(Me_5C_5), 40585-51-1; YbI_2, 31217-99-9; $EuBr_2$, 13780-48-8; Et_2O, 60-29-7.

Conversion of the Ketenylidene Cluster $[Fe_3(CO)_9(CCO)]^{2-}$ to the Acetylide Cluster $[Fe_3(CO)_9(CCOC(O)CH_3)]^-$ and Reactivity of the Acetylide System

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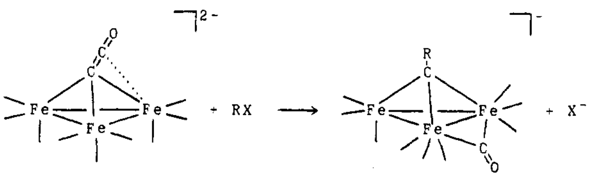
Summary: Acylation occurs at the oxygen atom of the ketenylidene moiety in $[Fe_3(CO)_9(CCO)]^{2-}$ to generate $[Fe_3(CO)_9(CCOC(O)CH_3)]^-$, which has been characterized spectroscopically and by single-crystal X-ray diffraction. The preservation of the C–C bond of the ketenylidene is noteworthy, and the product of this acylation reaction is the first acetylide cluster which contains an atom other than carbon or hydrogen adjacent to the C–C triple bond. Reactions with hydride and proton sources are described.

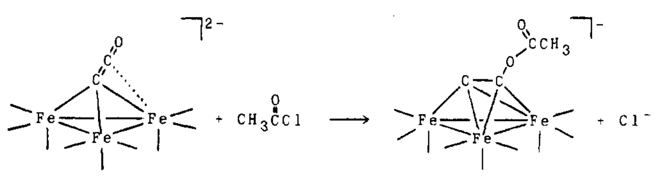
One important aspect of transition-metal cluster chemistry is the possibility of multi-metal bonding of ligands, which may activate bonds within the moiety or stabilize an otherwise unknown ligand.[1] The ketenylidene (C=C=O) ligand in the cluster anion $[Fe_3(CO)_9(CCO)]^{2-}$,[2] I, is an example of multi-metal ligand stabilization since the CCO moiety is unknown either in the free state or in monometal complexes. Earlier work demonstrated that in contrast to organic ketenes[3] or ketenyl ligands bound to a single metal center,[4] I reacts with protons or methylating agents at the α-carbon of the ketenylidene with subsequent C–C bond cleavage. The carbonyl group migrates onto the cluster framework affording II (eq 1).[2]



(1)

I

II a,b (a, R=H, X=CF_3CO_2; b, R=CH_3, X=I)



I III

(2)

In this communication, we report that I displays a second reaction pathway in which acetyl chloride attacks the ketenylidene oxygen without C–C bond cleavage and forms an acetylide cluster, III (eq 2). This cluster has been fully characterized spectroscopically and by single-crystal X-ray diffraction. We also report the reactivity of III toward hydride and proton sources.

When a CH_2Cl_2 solution of I is treated with acetyl chloride, a new compound, III, can be isolated in high yield.[5] Analytical and spectroscopic data indicate the formula $[PPN][Fe_3(CO)_9(CCOC(O)CH_3)]$.[6] On the basis of earlier work,[2] we expected a compound with structure II (R = $C(O)CH_3$) to be formed. However, there is no resonance in the ^{13}C NMR spectrum in the region associated with capping μ_3-CR groups, ca. 250–350 ppm.

The results of a single-crystal X-ray diffraction study of III show (Figure 1) that the acetyl group is attached to the ketenylidene oxygen.[7] This compound represents the product of the first example of reactivity at the oxygen atom of a cluster-bound ketenylidene moiety. Reaction 2 causes a change in bonding within the ligand from a four-electron donating ketenylidene (C=C=O) to a five-electron donating acetylide (C≡C—O). The analogous conversion of a π-bound ketenyl ligand to an alkyne has been observed in monometallic systems.[4] Clusters containing similar μ_3-(η^2-⊥)[11] bound acetylides are commonly synthesized from a terminal acetylene via C–H or C–X

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[4] Kreissl, F. R.; Sieber, W.; Wolfgruber, M. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 493. Kreissl, F. R.; Sieber, W. J.; Wolfgruber, M. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1983**, *38B*, 1419.

[5] In the preparation of III, 0.957 g (0.623 mmol) of I was dissolved in 5 mL of CH_2Cl_2 under an N_2 atmosphere. Acetyl chloride, 70 μL (0.98 mmol), was added and the solution stirred and then 25 mL of Et_2O was added and the solution filtered from [PPN]Cl. Solvent was removed, and the residue was crystallized from CH_2Cl_2/2-propanol; isolated 0.550 g, 85% yield. Pure material was recrystallized by slow diffusion of pentane into a CH_2Cl_2/Et_2O (1:2) solution of III.

[6] Anal. Calcd for $C_{49}H_{33}Fe_3NO_{11}P_2$: C, 56.52; H, 3.19; Fe, 16.09; N, 1.34. Found: C, 55.84; H, 3.28; Fe, 16.12; N, 1.35. IR: ν_{CO} (CH_2Cl_2) 2049 (w), 1990 (s), 1982 (s), 1961 (m), 1936 (m, sh), 1770 (w, br) cm^{-1}. ^1H NMR (CD_2Cl_2, +25 °C): 7.460 (m, 30 H, PPN^+), 2.296 (s, 3 H, $C(O)CH_3$). ^{13}C NMR (CD_2Cl_2, +25 °C): 216.1 (s, Fe–*C*O), 172.9 (s, *C*COC(O)CH₃), 168.1 (s, CCO*C*(O)CH₃), 132.2 (s, C*C*OC(O)CH₃), 20.6 (q, $^1J_{CH}$ = 130 Hz, CH_3) ppm, with ca. 0.03 M $Cr(acac)_3$ added. ^{13}C NMR (CD_2Cl_2, –90 °C) on a sample of III prepared from $[PPN]_2[Fe_3(*CO)_9(*C*CO)]$ (ca. 30% ^{13}C): 215.8 (s, 9 C), 171.6 (d on s, 1 C, $^1J_{CC}$ = 39 Hz), 130.8 (d on s, 1 C, $^1J_{CC}$ = 39 Hz) ppm, with $Cr(acac)_3$ added.

[7] Crystal data for III (–100 °C): triclinic; $P\bar{1}$; a = 10.934 (5) Å, b = 13.189 (7) Å, c = 17.075 (6) Å; α = 84.90 (4)°, β = 70.14 (3)°, γ = 85.97 (4)°; V = 2305 Å^3; D(calcd) = 1.500 g·cm^{-3}; Z = 2; $\mu_{MoK\alpha}$ = 10.593 cm^{-1}. Data collection: Enraf Nonius CAD4 diffractometer, graphite-monochromated Mo radiation, variable speed ω–2θ scans, $3° < 2\theta < 50°$, $\lambda_{MoK\alpha}$ = 0.71073 Å. Data (4425 with $I > 3\sigma(I)$) were corrected for Lorentz, polarization, and background effects.[8] An empirical absorption correction based on psi scans was performed. The structure was solved by direct methods (MULTAN,[9] DIRDIF[10]). Hydrogen atoms were input in idealized positions, C–H = 0.95 Å. Refinement of scale factor, positional parameters, and anisotropic thermal parameters for all non-hydrogen atoms converged to R_F = 4.440% and R_{wF} = 4.926%.

[8] All computations were performed on a VAX 11/730 computer with Enraf-Nonius SDP software and local programs.

[9] MULTAN 11/82 by P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J.-P. Declercq, and M. M. Woolfson.

[10] DIRDIF: Beurskens, P. T.; Bosman, W. P.; Doesburg, H. M.; Gould, R. O.; van den Hark, Th., E. M.; Prick, P. A. J. "Computational Crystallography"; Sayre, D., Ed.; Clarendon Press: Oxford, 1982.

[11] The notation μ_3-(η^2-⊥) signifies that the acetylide C–C bond is perpendicular to a metal–metal bond to distinguish from the case where the C–C bond is parallel to a metal–metal bond, μ_3-(η^2-∥). See ref 12.

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