

Supporting Information for the Paper Entitled:

“Oxidative Decarbonylation of *m*-Terphenyl Isocyanide Complexes of Molybdenum and Tungsten: Precursors to Low-Coordinate Isocyanide Complexes”

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S1. Spectroscopic Data for $\text{MoI}_2(\text{CO})_2(\text{CNAr}^{\text{Dipp2}})_2$

Shown in Figures S1 and S2 are the ^1H NMR and IR spectra of freshly prepared $\text{MoI}_2(\text{CO})_2(\text{CNAr}^{\text{Dipp2}})_2$ in C_6D_6 solution before crystallization from toluene at -35°C . The ^1H NMR spectrum is indicative of a single paramagnetic complex, while the IR spectrum in C_6D_6 indicates a *trans*-dicarbonyl isomeric preference (the splitting of the single peak is due to vibronic coupling with other modes). Figure S3 depicts a solid-state IR spectrum (KBr) of crystals of $\text{MoI}_2(\text{CO})_2(\text{CNAr}^{\text{Dipp2}})_2$. Relative to the solution spectrum (Figure S2), two additional peaks are present in the solid state. These two well-separated peaks are assigned to the *cis*-dicarbonyl of $\text{MoI}_2(\text{CO})_2(\text{CNAr}^{\text{Dipp2}})_2$. Figure S4 shows a room-temperature, solution IR spectrum (C_6D_6) of the toluene-grown crystals 20 min after dissolution. Near-complete regeneration of the *trans*-dicarbonyl isomer is observed.

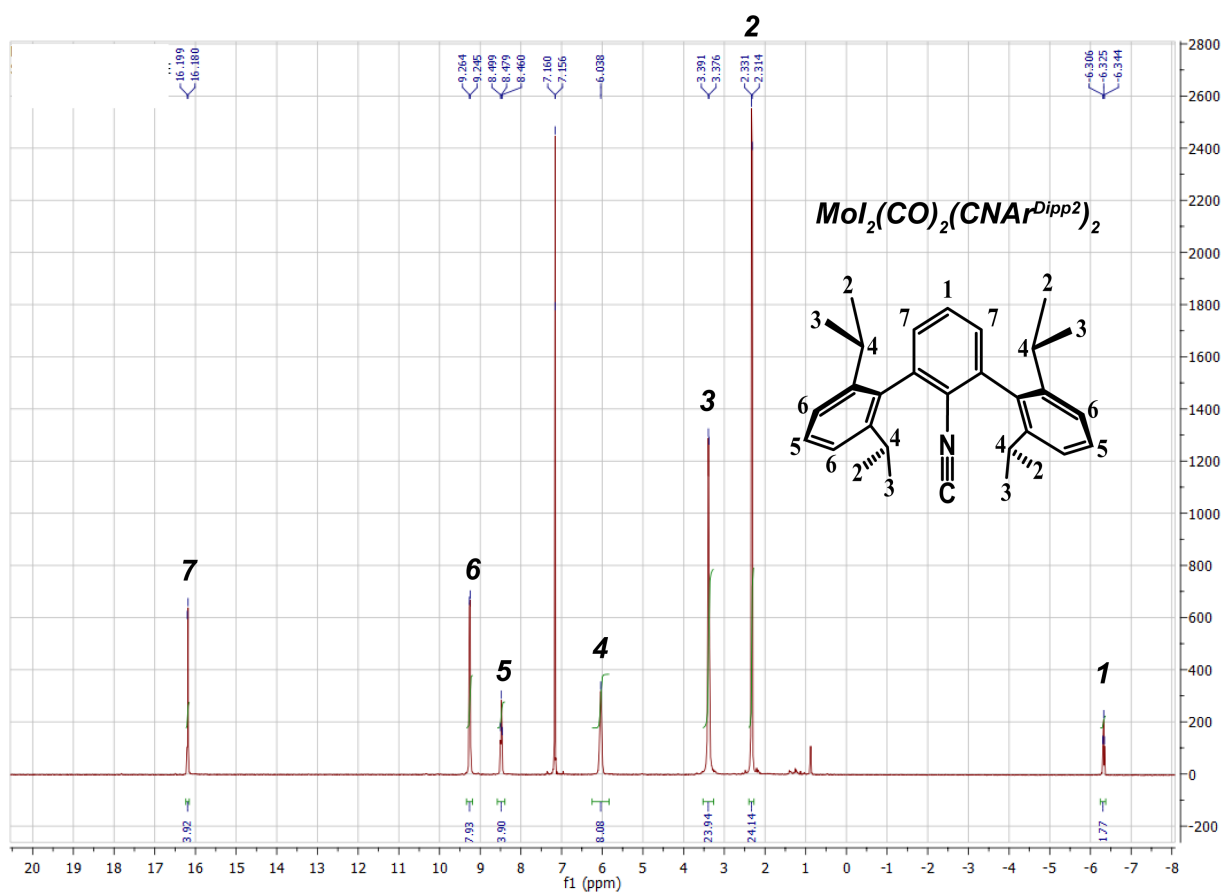


Figure S1. ^1H NMR spectrum (400 MHz, 20°C) of freshly prepared $\text{MoI}_2(\text{CO})_2(\text{CNAr}^{\text{Dipp2}})_2$ in C_6D_6 .

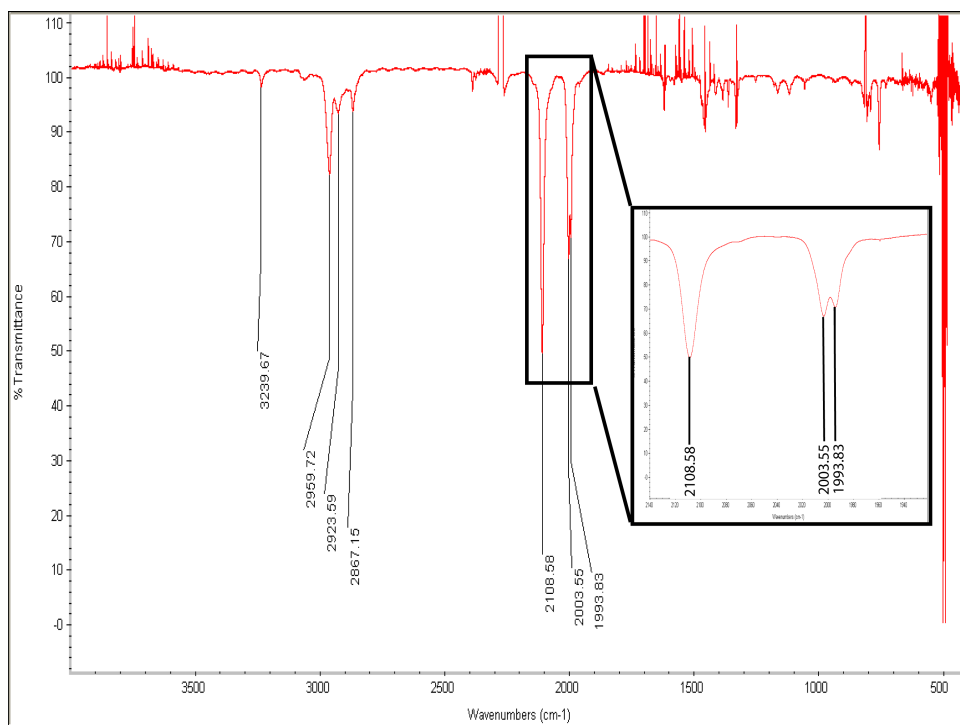


Figure S2. Solution FTIR spectrum (C_6D_6) of freshly prepared $\text{MoI}_2(\text{CO})_2(\text{CNAr}^{\text{Dipp}2})_2$. The presence of the *trans*-isomer is indicated from the $\nu(\text{CO})$ stretches (the splitting of this peak is due to vibronic coupling with other modes).

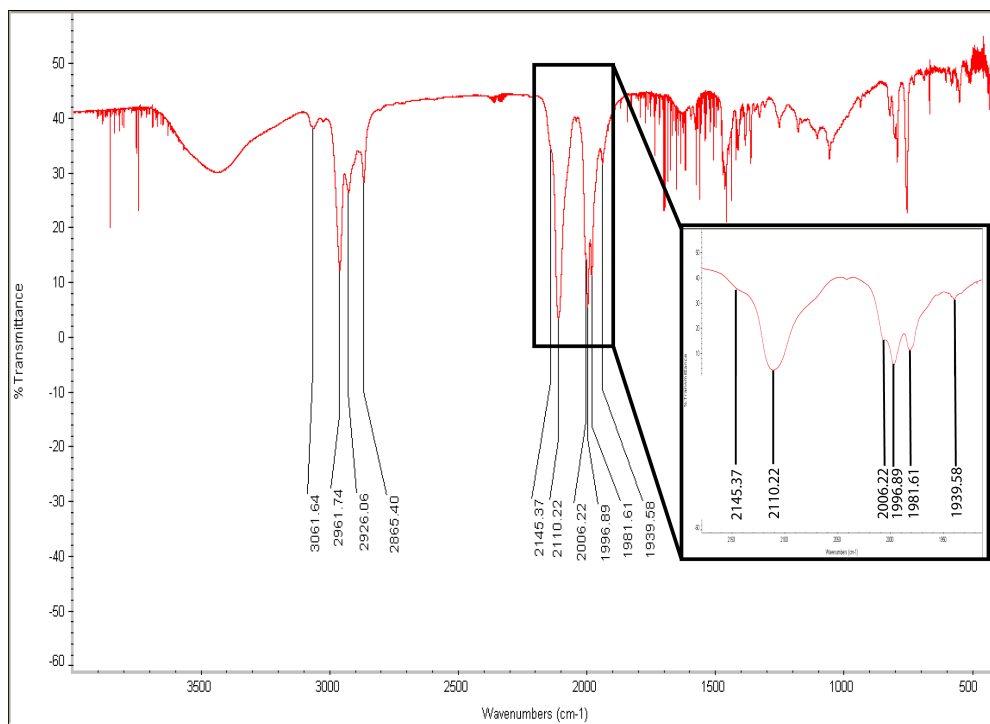


Figure S3. Solid-state FTIR spectrum (KBr) of $\text{MoI}_2(\text{CO})_2(\text{CNAr}^{\text{Dipp}2})_2$ crystals grown from toluene at $-35\text{ }^\circ\text{C}$. Both *cis*-dicarbonyl and *trans*-dicarbonyl isomers are indicated from the $\nu(\text{CO})$ stretches.

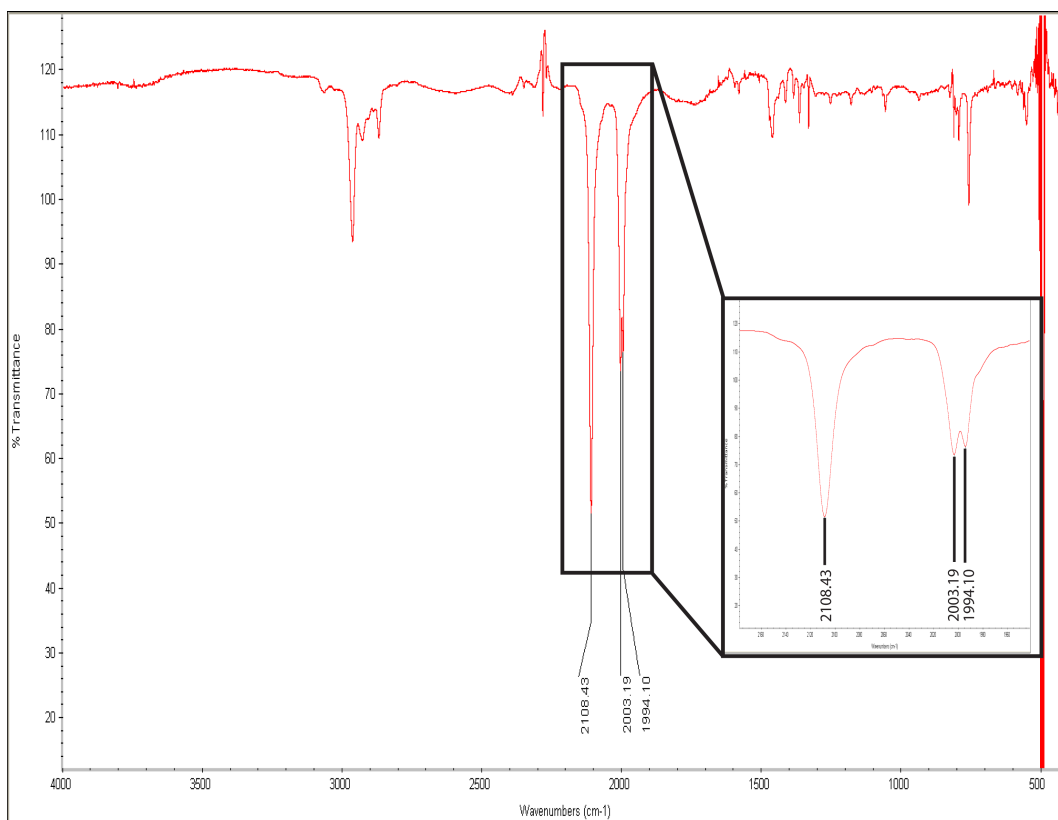


Figure S4. Solution FTIR spectrum (C_6D_6) of $\text{MoI}_2(\text{CO})_2(\text{CNAr}^{\text{Dipp}2})_2$ crystals grown from toluene at -35°C taken 20 min after dissolution. Near-complete regeneration of the *trans*-dicarbonyl isomer is indicated from the $\nu(\text{CO})$ stretches.

S2. Crystallographic Structure Determinations

General. Single crystal Xray structure determinations were carried out at low temperature on a Bruker P4, Platform or Kappa Diffractometer equipped with a Bruker APEX detector. All structures were solved by direct methods with SIR 2004¹ and refined by full-matrix least-squares procedures utilizing SHELXL-97.² Crystallographic data-collection and refinement information is listed in Table S1. The crystal structure of **1-W** contained positional disorder between one CO ligand and the coordinated acetonitrile molecule. The disorder was modeled such that both the CO and acetonitrile molecules are represented at 50% occupancy in each site. The crystal structure of **4** reveals co-crystallization of a 50/50 mixture of both the *cis*- and *trans*-dicarbonyl isomers. Both *cis*- and *trans*-dicarbonyl isomers contain whole molecule disorder and consequently the heavier Mo and I atoms were modeled and refined over several positions. Also, the *cis*-carbonyl isomer contains positional and compositional disorder between the CO ligands and terminal iodides within the equatorial plane of the molecule. The disorder was modeled such that the total of all ligand occupancy equals two CO ligands and two iodide ligands. The crystal structure of **7** contains isopropyl-group positional disorder, which was modeled and refined. The crystal structure of **10** contains positional disorder in one of the bound acetate ligands, which was modeled and refined. The crystal structures of **6** and **11** contain disordered toluene and $\text{O}(\text{SiMe}_3)_2$ molecules of co-crystallization, respectively. These disordered components were also modeled and refined.

Table S1. Crystallographic Data and Refinement Information.

	<i>trans</i> -W(NCMe)(CO) ₃ (CNAr ^{Dipp2}) ₂ •2CH ₂ Cl ₂ (1 -W•2CH ₂ Cl ₂)	<i>trans</i> -W(CO) ₄ (CNAr ^{Dipp2}) ₂ (2 -W)	WI ₂ (CO) ₃ (CNAr ^{Dipp2}) ₂ (3 -W)
Formula	C ₇₁ H ₈₅ Cl ₁₈ N ₃ O ₃ W	C ₆₆ H ₇₄ N ₂ O ₄ W	C ₆₅ H ₇₄ I ₂ N ₂ O ₃ W
Crystal System	Monoclinic	Monoclinic	Monoclinic
Space Group	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , Å	15.870(3)	24.073(2)	19.3808(7)
<i>b</i> , Å	10.825(2)	23.997(2)	17.0361(6)
<i>c</i> , Å	22.399(7)	21.1748(17)	20.8151(8)
α, deg	90	90	90
β, deg	109.563(6)	108.2280(10)	116.4150(10)
γ, deg	90	90	90
V, Å ³	3625.9(15)	11618.0(17)	6155.1(4)
<i>Z</i>	2	8	4
Radiation (λ, Å)	Mo-Kα, 0.71073	Mo-Kα, 0.71073	Mo-Kα, 0.71073
ρ (calcd.), g/cm ³	1.370	1.307	1.477
μ (Mo Kα), mm ⁻¹	1.933	2.036	2.924
Temp, K	100(2)	100(2)	100(2)
θ max, deg	28.45	25.05	28.27
data/parameters	8308/404	10770/663	14311/674
<i>R</i> _I	0.0484	0.0422	0.0538
<i>wR</i> ₂	0.1099	0.1230	0.1545
GOF	1.014	1.057	1.057

Table S1. Con't.

	MoI ₂ (CO) ₂ (CNAr ^{Dipp2}) ₂ (4)	MoI ₂ (THF)(CO) ₂ (CNAr ^{Dipp2}) ₂ (5)	<i>trans</i> -MoI ₄ (CNAr ^{Dipp2}) ₂ •(C ₇ H ₈) (6 •(C ₇ H ₈))
Formula	C ₆₄ H ₇₄ I _{1.95} MoN ₂ O ₂	C ₆₈ H ₈₂ I ₂ MoN ₂ O ₃	C ₇₈ H ₉₄ I ₄ MoN ₂
Crystal System	Monoclinic	Orthorhombic	Monoclinic
Space Group	<i>C</i> 2/ <i>c</i>	<i>Pbca</i>	<i>C</i> 2/ <i>m</i>
<i>a</i> , Å	24.3913(6)	27.6865(9)	20.601(5)
<i>b</i> , Å	24.3951(6)	17.4569(6)	16.167(4)
<i>c</i> , Å	21.1052(5)	29.1280(10)	15.491(7)

α , deg	90	90	90
β , deg	107.9900(10)	90	90
γ , deg	90	90	90
V , Å ³	11944.5(5)	14078.2(8)	4162(2)
Z	8	8	4
Radiation (λ , Å)	Cu-K α , 1.54178	Cu-K α , 1.54178	Mo-K α , 0.71073
ρ (calcd.), g/cm ³	1.387	1.250	1.327
μ (Mo/Cu K α), mm ⁻¹	10.044	8.718	1.678
Temp, K	100(2)	100(2)	100(2)
θ max, deg	70.87	65.24	27.14
data/parameters	10563/678	11666/701	4747/219
R_I	0.0601	0.0569	0.0416
wR_2	0.1816	0.1627	0.1196
GOF	1.070	1.054	1.084

Table S1. Con't.

	W(O ₂ CPh) ₂ (CO) ₂ (CNAr ^{Dipp2}) ₂ (7)	W(O ₂ CMe) ₂ (CO) ₂ (CNAr ^{Dipp2}) ₂ (8-W)	Mo(O ₂ CMe) ₂ (CO)(CNAr ^{Dipp2}) ₂ (9)
Formula	C ₇₈ H ₈₄ N ₂ O ₆ W	C ₆₈ H ₈₀ N ₂ O ₆ W	C ₆₇ H ₈₀ MoN ₂ O ₅
Crystal System	Triclinic	Triclinic	Triclinic
Space Group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
a , Å	16.1462(6)	12.7672(9)	10.8652(7)
b , Å	16.9570(6)	18.9332(14)	14.4040(9)
c , Å	25.6350(9)	26.1549(19)	21.3033(13)
α , deg	106.364(2)	94.5690(10)	109.3830(10)
β , deg	90.527(3)	90.2100(10)	93.6950(10)
γ , deg	91.057(2)	101.2740(10)	101.9650(10)
V , Å ³	6732.4(4)	6179.4(8)	3044.6(3)
Z	4	4	2
Radiation (λ , Å)	Cu-K α , 1.54178	Mo-K α , 0.71073	Mo-K α , 0.71073
ρ (calcd.), g/cm ³	1.312	1.295	1.188
μ (Mo/Cu K α), mm ⁻¹	3.597	1.920	0.264
Temp, K	100(2)	100(2)	100(2)

θ max, deg	68.65	28.33	25.37
data/parameters	22977/1578	28160/1424	11135/694
R_I	0.0446	0.0370	0.0388
wR_2	0.0941	0.0923	0.1084
GOF	1.025	1.004	1.074

Table S1. Con't.

	<i>trans</i> -MoI ₃ (THF)(CNAr ^{Dipp2}) ₂ (10)	(η^6 -C ₆ H ₆)Mo(N ₂)(CNAr ^{Dipp2}) ₂ • ((Me ₃ Si) ₂ O) (11 • (Me i) ₂ O)	(η^6 -C ₆ H ₆)MoI ₂ (CNAr ^{Dipp2}) ₂ (12)
Formula	C ₆₆ H ₈₂ I ₃ MoN ₂ O	C ₇₁ H ₈₉ MoN ₄ OSi ₂	C ₆₈ H ₈₀ I ₂ MoN ₂
Crystal System	Tetragonal	Triclinic	Monoclinic
Space Group	<i>P</i> 4 ₃ 2 ₁ 2	<i>P</i> -1	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , Å	17.956(6)	12.5493(10)	15.891(9)
<i>b</i> , Å	17.956(6)	12.7014(11)	18.193(10)
<i>c</i> , Å	41.03(2)	22.4890(19)	22.629(12)
α , deg	90	74.1840(10)	90
β , deg	90	74.6450(10)	110.253(7)
γ , deg	90	68.8530(10)	90
<i>V</i> , Å ³	13229(9)	3160.8(5)	6137(6)
<i>Z</i>	8	2	4
Radiation (λ , Å)	Mo-K α , 0.71073	Mo-K α , 0.71073	Mo-K α , 0.71073
ρ (calcd.), g/cm ³	1.402	1.188	1.380
μ (Mo K α), mm ⁻¹	1.637	0.271	1.260
Temp, K	100(2)	100(2)	100(2)
θ max, deg	27.29	25.35	25.44
data/parameters	14759/674	11568/722	11234/674
R_I	0.0640	0.0643	0.0353
wR_2	0.1519	0.1793	0.0836
GOF	1.021	1.026	1.027

- [1] Burla, M. C.; Caliendo, R.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; De Caro, L.; Gaicovazzo, C.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **2005**, *38*, 381–388.
- [2] Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112–122.